INVASIVE SPECIES AND PANNE ECOSYSTEMS: THE EFFECTS OF ATMOSPHERIC POLLUTION

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ABSTRACT

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Pannes are rare intradunal wetlands. Though small, they are known to exhibit extremely diverse and sensitive vegetation and are home to a number of reptile and amphibian species. In the United States, pannes are known to occur only around the Great Lakes Basin and Cape Cod. At Indiana Dunes National Lakeshore, the fifteen known pannes have an unusually large variety of plant species for such a small geographic area and provide habitat for plant species found nowhere else in Indiana. However, these sensitive ecosystems have been exposed to over a century of atmospheric pollutants from the surrounding steel and coal industries. Since 1986, the native vegetation of the area is slowly being replaced by invasive species like *Phragmites australis* and *Typha spp*. This study attempts to explain the shift in vegetation. Pannes in two other locations, at a distance from the industrial complex, were used as control sites as they were not expected to be exposed to the same levels of heavy metal concentrations.

Four of the fifteen pannes at the Indiana Dunes National Lakeshore, two of the four pannes at Sleeping Bear Dunes National Lakeshore, Michigan, and two of the three pannes at Warren Dunes State Park, Michigan, were studied, resulting in a total of eight pannes. The pannnes were stratified and sampled by hydroperiod. Surface soil samples

and sediments at depth, were recovered from each of the pannes considered in this study and analyzed for heavy metal, phosphorus, carbon and nitrogen content.

Results show that high levels of organic matter coupled with high nutrients and high metals, in the soil, are a combination that may be considered a risk factor for future invasion of pannes by invasive species. It appears to be difficult for the native vegetation to deal with the high metals and high nutrients which are deleterious to the native vegetation and facilitate establishment of invasive vegetation which is more tolerant to the altered geochemical conditions.

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1.0 INTRODUCTION

Indiana Dunes National Lakeshore (known in the National Park System as INDU), is located at the southern tip of Lake Michigan. It is downwind of the Chicago - Hammond - Gary area, historically one of the most industrialized regions of the United States. Thus INDU has been subjected for over a century to high rates of airborne heavy metal and nutrient deposition and accumulation, which has impacted local and regional ecosystems. The INDU has considerable floristic diversity for the upper Midwest (NPS, PMIS# 71530). At 15,000 acres (~6000 hectares), it is one of the smaller national parks, but it ranks third in terms of floristic diversity (NPS, 2007). The park is an ecotone where the ranges of boreal, prairie, deciduous forest and savanna/woodland species all overlap, and where coastal species, a relict of past plant migrations, remain in unique niches. Given the importance of the species richness in this region, it is surprising that few studies have been conducted on the effects of atmospheric derived pollutants on the flora of the INDU. Wetmore (1989) suggests that air pollution may have resulted in the mortality of lichens. An ongoing study by Greg Mueller of the Chicago Field Museum suggests that elevated levels of nitrogen deposition may be related to smaller proportions of ectomycorrhizae (a distinct type of fungus root symbiosis) present at INDU than at comparable nature preserves in the Chicago area (NPS, 2007). However, there have been no studies of the effects of atmospheric derived pollutants on the vascular vegetation or on ecosystem process such as native plant or invasive plant recruitment.

One relatively rare feature within the INDU, are small nutrient limited intra - dunal/upland complexes known as pannes. These pannes provide habitat for many habitat - restricted plants as well as sensitive amphibian, reptile and dragonfly species. However, over the past 20 years cattail, common reed, and other invasive species have established themselves in the pannes, raising concerns about long - term species diversity and ecological health of the INDU. The pannes are considered a globally imperiled community by the Nature Conservancy and have been placed on the second tier of conservation targets by the Chicago Wilderness Biodiversity recovery plan (EPA - Biodiversity Recovery Plan, December 1999).

This study, part of a broader field and experimental mesocosm, multi - disciplinary investigation of the pannes and their vegetation, focuses explicitly on the impacts of historical heavy metal and nutrient deposition on the pannes and distribution of the invasive species developing within them. Insight into the structure and dynamics of pannes, and the effect of heavy metal deposition, has important implications for future predictions of natural communities and the management of natural areas.

1.1 Pannes

Pannes are calcareous or carbonate rich depressions that form near the water table in intra - dunal areas (EPA - Biodiversity Recovery Plan – Chicago Wilderness Terrestrial Community Classification System, December 1999). Pannes are nutrient limited and small; generally not more than 3 - 4 acres (1 - 1.5 hectares) in area. What makes them so unique is their species richness (Hiebert et al., 1986). Pannes are rare ecosystems known to occur around the Great Lakes Basin in the Midwest, USA. They are scattered along the eastern and southern dune systems of Lake Michigan, the southern shore of Lake Huron, and one known location on Lake Superior (Hiebert et al., 1986).

Similar isolated wetlands, which have been formed due to aeolian processes, are abundant along the sand dunes at Cape Cod, Massachusetts (Tiner, 2003). Dune slacks, features comparable to pannes, associated with marine dune sediments, are found in the Netherlands, North Wales and North Devon, England, New South Wales, and Australia (Hiebert et al, 1986). Ewanchuk and Bertness (2004) have studied numerous forb pannes among the northern New England salt marshes. These forb pannes, though different from the pannes around the Great Lakes in that they are saline, are areas of high species diversity, comparable to the pannes in the Midwest.

Within a mile (<2km) of the southern tip of Lake Michigan, along the Indiana Dunes National Lakeshore, are the series of pannes which are the focus here. The pannes are small (1 - 4 acres; <1.5 hectares) upland/wetland complexes, of which 80 - 90% is wetland. Each panne is completely surrounded by high dunes and is defined by the perimeter described by the base of the dunes (Figure 1). No surface water enters the pannes. Thus, the hydrology is a function of precipitation and a seep zone. In the INDU pannes, this seep zone is located to the southwest edge of the pannes. Water will pool in the lower portions of the panne (at the INDU upto a depth of 0.7m in the summertime, Dan Mason, personal communication). The exact origin of pannes is not known, but it has been speculated, that the pannes were created by the aeolian processes around the turn of the century, a period during which groundwater levels and water levels in Lake Michigan were comparatively low (Dan Mason, personal communication). The lake levels rose in the 1930s, in turn raising the water table, which was exposed as standing water in the base of the depressions (Figure 2).

The 15 known pannes at INDU make up about 0.3% of the INDU's total area. The variety of species and habitat is unusually large for such a small geographical area (Dan Mason, personal communication). INDU ranks third amongst national parks in floristic richness, providing habitat to over 1,400 different plant species. The pannes at INDU have 213 known plant species in their 55 acres, 17 of which are state listed endangered plants (12.6% of state - listed plant species at INDU). More than twenty years ago, Hiebert and Wilcox (1986) conducted a study of vegetation patterns in five of the fifteen pannes at INDU investigating the relationship between species composition, water chemistry and water depth/depth to water table. It is interesting to note that no invasive plants[1] were noted at that time. However, more recent investigations (Dan Mason, personal communication, 2004) have documented the presence of exotic invasive species such as *Phragmites australis* (Common Reed), *Phalaris arundinaceae* (Reed Canary Grass), *Typha* spp (Hybrid Cattail), *Lythrum salicaria* (Purple Loosestrife) and *Salsola kali* (Russian Thistle) in some of the pannes. The most common of these are the Hybrid Cattail and Common Reed. In one panne, three state listed species present in the 1980s are now extinct (Dan Mason, unpublished National Park Service data, 2004). In 50% of the pannes, exotic species are sufficiently dense to have a notable negative impact on native panne vegetation. Yet in other pannes, invasives are not evident.

[1] An exotic species is a non - native introduced species which does not necessarily have a negative effect on the ecosystem on which it is introduced. An invasive species, in contrast, is a non negative species whose introduction is likely to cause economic or environmental harm or harm to human health. Hence all invasive species are exotic species, but not all exotic species are invasives. An invasive species generally out - competes native species for space and resources, thereby reducing biodiversity in the area (U.S. Environmental Protection Agency, April 2007).

Why certain pannes at the INDU have been colonized by invasives is not known. The seeds of Hybrid Cattail and Common Reed (the prevalent invasive species found in the pannes) are characterized by leaf like appendages that facilitate wind dispersal. Hybrid Cattail was first described in this region around 1960, but it is likely that they were present for some time before, although due to the absence of appropriate germination conditions and/or growth limitations, they were unable to establish. However, another explanation could be that invasive species did not arrive in abundance in the airshed of INDU before 1960, and thus it was not likely until then that there were enough seeds of invasive species to land in sites conducive to their growth (NPS, PMIS# 71530).

Regardless of the reason for the appearance of invasives in the pannes at the INDU, one of the remaining critical issues is why some pannes remain free of invasives even though they are in close proximity to those pannes that have been successfully colonized. We suggest this is probably due to difference in panne environments. Studies have documented that atmospheric pollutants such as heavy metals and nitrogen increase the susceptibility of vegetation to invaders (Rand and Louda, 2003). Thus a second explanation for the presence of invasives in the pannes is linked to the accumulation of airborne pollutants (metals and nutrients) which has reduced the resistance of the panne vegetation to invasive species. This second hypothesis is the one tested here.

1.2 Effect of Heavy Metal Loading

Pannes are isolated hydrological features, with no inflowing streams. Thus dissolved metal and nutrient inputs from groundwater and direct deposition from the atmosphere are the two main sources of heavy metals in panne ecosystems.

As noted above, the Indiana Dunes National Lakeshore lies downwind of the Chicago - Gary - Hammond industrial area, historically one of the most industrialized regions in the United States. The steel producing mills and coal plants were first built in this region in the 1860s and grew rapidly and extensively thereafter (Botts, 1993). As recently as the mid 1990s, this area was responsible for 25% of the steel manufactured in the United States (Botts, 1993). In addition to steel manufacturing, coal, coke and fuel oil combustion, casting and coating, plating and polishing, woodworking and the production of inorganic pigments augment the atmospheric pollutant load along this shoreline (Winchester and Nifong, 1971; Cole et al., 1990; USEPA 1995; Souch et al., 2002).

Thus the INDU has been subjected to over a century of airborne deposition of heavy metals. Studies have confirmed elevated levels of heavy metals in the Great Marsh, an inter - dunal wetland with organic rich soils (NPS, PMIS# 71530), and across organic - rich soils of northwestern Indiana (Parker et al., 1978; Miller and McFee, 1983). The average pH of rainfall in the INDU is 4.5, amongst the most acidic in the United States (NADP, 1998). Manganese (Mn), Zinc (Zn), Barium (Ba), Nickel (Ni) and Chromium (Cr) are typically emitted from steel mills, while Copper (Cu), Lead (Pb) and Zinc (Zn) are typically derived from the combustion of fossil fuels (Table 1). Although there is stratigraphic evidence for post - depositional mobility, the wetlands retain significant quantities of heavy metal inputs in their upper profiles (Dollar et al., 2001). Metal depositional rates have been elevated over background rates for this region and although rates of deposition have dropped recently, given how strongly many metals are retained in the wetland sediments, concentrations have continued to rise.

Elevated levels of heavy metals, for example, Cd, Pb, Cu, Zn, Cr, Ni, and Mn can be toxic to plant cells. These metals can stunt growth, cause chlorosis, reduce germination, reduce growth rates and alter nutrient uptake (Bazzaz et al., 1974; Root et al., 1975; Lee et al., 1976; Barua and Jana, 1986). Thus elevated heavy metals can result in a shift in wetland plant community structure (NPS, PMIS# 71530).

1.3 Effect of Nutrient Enrichment

Plants require many nutrients to grow: Nitrogen (N), Phosphorous (P), Potassium (K), Calcium (Ca), Magnesium (Mg), Sulfur (S), and Iron (Fe), for example. Of these, N and P are needed in relatively large quantities. Competition for nutrients is strong amongst plants, but the excess of one nutrient cannot make up for the deficiency of another.

In the pre - industrial world, the dominant nitrogen source for aquatic and terrestrial ecosystems was derived through natural biological processes, notably N - fixing. Generally, natural processes produced less nitrogen than demanded by terrestrial and aquatic ecosystems and these ecosystems evolved within the nitrogen - limited environment. By 2001, however, human activities were responsible for releasing 15 times more nitrogen into the environment than in 1860 (Cowlings, 2001). This has resulted in many ecosystems having a surplus of nitrogen and plant assemblages being dominated by a few nitrophilious species. Examples of species - rich wetlands becoming species poor and dominated by a few exotic species are common in the literature (Ehrenfeld, 1983; Aerts and Berebdse, 1988; Verhoeven et al., 1993).

Data collected as part of the National Acid Deposition Program (NADP) shows that the northwest portion of Indiana and the western border of Michigan have some of the highest rates of nitrogen deposition rates in the United States (Figure 3). Between 1981 and 2001, for example, the average annual wet deposition of ammonium was 3.93 kg per hectare and that of nitrate 16.3 kg per hectare. One source of nitrogen is from the combustion of fossil fuels. This in combination with agricultural activities in the region and nitrogen fixation, is responsible for nutrient enrichment of the area.

Phosphorus is an important plant nutrient. P applied directly to fields to increase crop yields has become the dominant source of P in the P cycle. The early source of fertilizer P was from rock phosphate, which was ground and applied to fields, where it significantly enhanced crop yield. Along with enriching the P content in the fields, the P - rich rock was also rich in Cadmium and Uranium, which are both toxic to plants (Schlesinger, 1997), and which left many previously productive fields barren. This, in turn, led to the development and perfection of a variety of leaching techniques to separate the beneficial P from the toxic heavy metals. The Green Revolution followed. However, the irony of the Green Revolution has become apparent, as the production of enormous amounts of food fueled by fertilizers to feed a growing global population has caused a variety of detrimental environmental conditions, including eutrophication of surface water supplies, significant soil loss, and expanding coastal “dead zones”. These regions of hypoxia and fish mortality are likely caused by fertilizer runoff from agricultural practices.

Nutrient rich environments are known to be more favorable to the invasive species Hybrid Cattail and Phragmites, which are found in abundance in some of the pannes at Indiana Dunes (Newman et al., 1997; Rickey et al., 2004).

1.4 Objectives

The aim of this study is to investigate the effects of heavy metals and excessive nutrients on the vegetation in the pannes at INDU, through geochemical analyses of underlying sediments. The approach taken is to study four pannes at the INDU which exhibit different levels of abundance of invasive species and to compare the results with those from four additional pannes that serve as controls at locations more distant from the industrial sources of the Chicago - region (at Warren Dunes and Sleeping Bear Dunes). Specific questions that are addressed include:

1. Are there differences in heavy metal and nutrient levels among pannes at the Indiana Dunes National Lakeshore?
2. If there are differences, how do these relate to the organic matter content of the sediments? Is the metal/ nutrient relationship similar to that for other wetland environments at the Indiana Dunes National Lakeshore documented by previous studies?
3. Do pannes at Indiana Dunes National Lakeshore exhibit higher levels of heavy metals and nutrients than pannes on the eastern shore of Lake Michigan (Warren

Dunes, Michigan, and Sleeping Bear Dunes, Michigan) where atmospheric deposition of pollutants is less?

4. Do levels of heavy metals and nutrients have a spatial component within a panne or are pollutants uniformly distributed across a panne?
5. Is there a relationship between heavy metal and nutrient levels found within a panne and the quantity and distribution of invasive species?

Pannes are unique features on the dune landscape. Their limited hydrological inputs, tight nutrient cycles, geographic isolation, and heterogeneous composition, make them highly diverse and sensitive to disruption. If heavy metals and nutrients are spatially distributed in the pannes in accordance with definable physical or geochemical features, and if the presence of these pollutants are linked to the distribution of invasives, then park managers at the INDU, and similarly affected sites elsewhere, will be able to easily identify 'hot spots' of susceptibility in the pannes and implement corrective management activity before establishment of an invading plant.

Given the multiple possible controls on invasive species at these sites, it is important to briefly describe other ongoing studies associated with this project. Notably, questions related to the rates at which invasive propagules are arriving at the pannes and relationships with past rates are being investigated through seed bank and seed rain studies, being conducted by the Indiana Dunes National Lakeshore (Dan Mason). The critical threshold accumulation rates for nutrients to generate safe sites for the establishment of Hybrid Cattail in nutrient limited sand based wetlands are being considered through mesocosm experiments.

The effects of lake levels on the abundance of invasives is not considered further here because this hypothesis was difficult to support. It is clear that the lake levels have dropped post 1986 (Figure 2), and this has certainly changed the hydrology and water table in the surrounding pannes, but this alone cannot guarantee more hospitable conditions for invasives, without further research.

2.0 STUDY SITE

The primary site of interest in this study is the Indiana Dunes National Lakeshore which is located along approximately 30 km of the southern shore of Lake Michigan, in Lake County and Porter County in Northwest Indiana (Figure 4, 5a and 5b). The Indiana Dunes National Lakeshore was established by U.S. Congress in 1966. The geomorphology of INDU is best characterized as a repeated series of dune ridges and wetland swales resulting from sequential retreats of the Wisonsinan glaciers and subsequent changes in lake levels (see Thompson and Baedke, 1997). Just inland from the second row of beach dunes is a series of blowout depressions which contain pannes ranging in size from several square meters to about 1 hectare (2.47 acres, latitude 41.557 N, longitude - 87.238 W) (Figure 6). The pannes vary in morphology, but are characterized by a steep north bank of sparsely vegetated sand and a more gradual southern slope with north - flowing seeps. (Hiebert et al., 1986). At the edge of the intradunal pond, the vegetation changes abruptly from the xeric dune vegetation to concentric bands of wetland vegetation the structure and composition of which are strongly influenced by small differences in topography and thus water level/depth to water table.

Of the fifteen pannes on the West Beach unit, four pannes were selected for detailed investigation. These pannes were selected because they encompass the entire variance in observable physical features of pannes at INDU and also extend along the entire length of shoreline where pannes occur. Of these pannes - herein referred to as panne 2, panne 3, panne 6 and panne 9 (see Figure 6), panne 2 is considered to be the most pristine (based on contemporary vegetation composition), and panne 6 is the most disturbed (with visually the greatest number of invasive species).

In addition to the pannes at the INDU, two pannes at each of two sites farther from the industrial sources of pollutants also were studied: Sleeping Bear Dunes National Lakeshore (NW Michigan) and Warren Dunes State Park (SW Michigan) (Figure 7a and 8a respectively). Sleeping Bear Dunes National Lakeshore stretches for about 60 km of Lake Michigan's western coastline and has four known pannes. These occur at the southern most tip of the park boundary, in Benzie County (latitude 44.41 N; longitude - 86.05 W). This area was designated a National Park in 1977. Two of these four pannes were studied (Figure 7b). Warren Dunes State Park extends along 5 km for approximately 1950 acres of Lake Michigan's southwest shoreline in Berrien County (latitude 41.79 N, longitude - 86.73 W). Two of the three pannes were studied (Figure 8b). These pannes were chosen because of easy access.

All of the pannes studied exhibit very clear internal stratification in terms of topography (elevation), hydrology (presence of open water/depth to water table) and vegetative characteristics, which are strongly inter related. Notable differences do occur in each of the pannes, for example in the extent of the seep zone and extent of the wetland habitat. The strongest natural control on species distribution within the panne is water depth/elevation above the water level (Hiebert et al., 1986). For this study, the vegetational stratification in each panne was found to be defined by visible differences in plant communities and composition and indicative of three hydro - geomorphic ecological units (permanently inundated, periodically flooded, never flooded but permanently under the influence of groundwater with different variations in water content in the soil). These hydro - geomorphic ecological units were then used as the basis for selecting the multiple samples of panne sediments for geochemical analysis. More details on the contemporary vegetation and the internal ecological structure of each of the pannes is the focus of a concurrent investigation (Dan Mason, personal communication).

Previous studies (Hiebert et al., 1986) documented that all the water analyzed from the pannes is high in Calcium - Magnesium Bicarbonate with pH values consequently well above neutral, ranging from 7.35 to 8.98. This is typical of groundwater - fed aquatic systems in the Indiana Dunes area. Other studies at the INDU (Perkins et al., 2000; Dollar et al., 2001) have noted the importance of standing surface water in neutralizing effects of the regional acid precipitation. Hiebert et al., (1986) note that while the calcareous water chemistry of the pannes probably influences which plant taxa occurs there, it is unlikely that water chemistry influences the distribution of species within the panne community because most of the variation is temporal rather than spatial. Table 2, lists the prominent industries in the Gary, Indiana region and its approximate distance from the INDU.

3.0 METHODS

The primary objective of this study is to document the spatial distribution of atmospherically derived heavy metals and nutrients in the sediments of eight pannes.

The samples recovered from the pannes were analyzed for organic matter content (substances made up primarily of carbon, oxygen, hydrogen and nitrogen), Iron (Fe), Cadmium (Cd), Chromium (Cr), Copper (Cu), Manganese (Mn), Barium (Ba), Zinc (Zn), Lead (Pb), Nickel (Ni), Sulfur (S) and Phosphorus (P) using strong acid digestion. A sequential P extraction was also carried out on the samples, in order to isolate the four fractions of P. Amounts of major nutrients such as nitrogen (N) and carbon (C) were also determined. The following sections talk about field and laboratory methods in detail.

3.1 Field Methods

Soil samples were collected at 15 - 20 sites in each of the eight pannes during the summer of 2004 (May - August). The sites were selected to represent the different hydro - geomorphic ecological units in each of the pannes, inundated, periodically inundated, and dry. The samples were collected using a 7” sterile sample scoop (Figure 9). The samples extended to a depth below active soil development, which varied across each of the pannes (sample depth ranged from 5 to 15 cm). Random replicates were also recovered from each panne to assess reproducibility. The samples were transferred into 18 oz (1.122 lbs) whirl - pak bags and sealed. Once brought back to the laboratory, the samples where refrigerated and stored until ready for analysis.

In the field, when the samples were collected, temperature, pH, salinity, conductivity and dissolved oxygen of the ground water (where exposed), were measured using a Hydrolab^{TM} multi parameter probe. In addition, soil cores from each hydro - geomorphic ecological unit, in each panne were also recovered temporarily and the structure of the sediments (depth of units, color, grain size) described.

3.2 Analytical Methods

All analyses of the sediments were carried out in the Geochemical Lab, Department of Earth Sciences, Indiana University - Purdue University Indianapolis. In addition to the samples collected, random replicates were also run for all analyses carried out to assess reproducibility.

3.2.1 Loss - On - Ignition

In order to determine organic matter content (OM% of mass), loss on ignition (LOI) was determined. A known weight of each sample (3 - 5g) was put into previously weighed acid cleaned watch glasses and dried in a oven at 60ºC for 2 - 3 days. Each watch - glass was then cooled in a dessicator and reweighed. The difference in weights gives the moisture content. Then, 1g of the dried samples was transferred into an acid cleaned ceramic crucible and ashed in a muffle furnace at 550ºC for 2.5 hours. In turn, each sample was cooled in a dessicator and reweighed to enable the calculation of the LOI organic matter content.

3.2.2 Strong Acid Digestion

In order to determine concentrations of metals in the samples, the ashed sample residues were transferred to 50ml polypropylene centrifuge tubes and treated with 40ml of 2N trace metal grade HCl. This strong acid digestion was carried out for 24 hours with orbital shaking (300rpm) at room temperature. The samples were then centrifuged for 15 mins at roughly 4275 rpm. About 0.6ml of the centrifuged samples were diluted with 6ml of milli - q water and then run through a Leeman Labs P950 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP - AES) fitted with a CETAC AT5000+ ultrasonic nebulization system, to obtain the total elemental concentrations of the samples. The ICP - AES determines the concentration of elements by measuring the intensity of light emitted by samples aspirated into an argon gas plasma heated to 10000ºK. Table 3 lists the detection limit and analytical reproducibility of the ICP - AES, indicating that the relative errors on each measurement are below 2% for Zn, Mn, Ba and Fe; are below 5% for Cd, Cu, P and Cr; are below 7% for Pb and Ni and is about 9% for S.

3.2.3 Sequential Phosphorus Extraction

During sample recovery, a thin red line was noticed in the soil samples recovered from the periodically inundated zone, in the pannes sampled at Indiana Dunes, showing that the red line could be due to the presence of Fe. In order to show if Fe played a role in nutrient cycling in the area and in order to determine the geochemical fractionation of phosphorus in the sediments, the Sequential Phosphorus Extraction was carried out on the samples recovered from the four pannes at Indiana Dunes: a total of 72 samples, including replicates and a laboratory Standard Reference Material 1646a

(SRMs - estuarine sediment). The SRMs were used to assess precision. The Sequential Phosphorus Extraction procedure used is outlined in Ruttenberg (1992) with modifications of Anderson and Delaney (2000). The premise is that different solid phases of P show dissimilar reactivity towards different solutions. Four phases of P are extracted using different extractants of various strengths so that the most reactive phases are removed first. (Table 4). Approximately 0.1g of sample was transferred into 15ml polyethylene centrifuge tubes. The first phase that was separated out is the occluded phase, which includes oxide associated P, bound to Fe, and the extraction was accomplished with a Sodium Citrate Dithionite Bicarbonate solution. The second phase extracted was the authigenic/ Carbonate mineral phase, which includes the P that was formed in place, after deposition. The chemical used here was Na - acetate buffered to pH ≈ 4. The third phase studied was the detrital phase which comes from particles formed from detritus. The fourth and final phase was organic P which used HCl and $MgNO_3$ for the extraction.

The extractions from steps 2, 3 and 4 were then analyzed for P concentrations, using a Shimadzu scanning UV - Visible Spectrophotometer, by means of the molybdate blue technique for color development. (Strickland and Parsons, 1968). The P, Fe and Mn concentrations from the Citrate Dithionite Bicarbonate solution were determined using the ICP - AES to avoid interference from the color developing solution.

3.2.4 Determination of CHN values

In order to quantify per cent concentrations of carbon, hydrogen and nitrogen in the solid samples from the pannes, a Flash EA 1112 Elemental Analyzer was used. A total of 170 samples, from all the pannes, in addition to standards and replicates were run. Samples (20 - 25mg) that had been previously dried and sieved were weighed and placed in tin cups, with vanadium oxide (5 - 10mg), which acts as a catalyst. An auto sampler is connected to a quartz reactor housed in a furnace at a temperature of 900ºC. Controlled amounts of Helium and oxygen are allowed to flow through the system. When the analysis starts, a valve allows oxygen to flow to a combustion reactor. The tin cup drops into the combustion reactor and tin comes in contact with the extremely oxidizing environment and triggers a strong exothermic reaction. Temperatures rise to approximately 1800ºC instantly causing the sample to combust. The electrical signals generated by the detector from gases flowing through the machine are processed by the Eager 200 software and provide nitrogen, carbon and hydrogen percentages. Percent error and typical detection limits for the CHN Elemental Analyzer are given in Table 5 and 6 respectively.

3.2.5 Statistical Calculations

Several statistical tools were used to analyze the data and assess significance. Straight forward tools like averages were useful for identifying general data characteristics (e.g. high values versus low values). Averages are used here across zones of pannes to examine differences, but ranges are also reported, and as is the case for much natural data, ranges sometimes overlap averages when comparing between zones.

Cross correlation analysis was also used. This analysis can reveal relationships between, in this case, elements, which is useful for identifying sources on cycling of the elements. The significance of the correlation between elements is evaluated by the correlation coefficient (r), which varies mathematically between - 1 (a perfect anti correlation) and +1 (a perfect correlation). This value reflects the distance between the modeled linear relationship and the actual data points. I used a transformation to r^2 which provides more statistical significance for data sets with a lower number of samples. Correlation coefficients (r^2) above about 0.3 indicate some degree of relationship between elements, with values closer to 1 indicating a very strong relationship. This is dependent on sample size considered. Approximately 1g of sample was ashed in a muffle furnace and the remaining sample weight was treated with HCl and run through the ICP - AES.

4.0 RESULTS

Results are presented in two primary sections with several subsections. The first section discusses the results obtained for the relationship between organic matter and nutrient enrichment. Secondly, heavy metal distribution at the three sites in this study, and its relation with organic matter is discussed in detail.

4.1 Organic Matter and Nutrient Enrichment

Soil organic matter is that fraction of the soil that is composed of plant and animal remains in various stages of decomposition. Organic matter is an indispensable component of all soils, as it is responsible for storing and supplying important nutrients such as nitrogen, carbon and phosphorous, which are needed for the growth of plants and soil organisms. Table 7 lists the organic matter percents for all the eight pannes considered in this study, including the highest, lowest and average organic matter and Table 8 lists the organic matter percent from the different hydrological zones. The nutrients considered in this study show a correlation with organic matter content, based on cross correlation. Those pannes with higher organic matter content appear to have higher concentrations of nutrients. All the pannes in this study show that there is a positive trend between total carbon and organic matter content (Figure 11a) and organic carbon and total nitrogen. (Figure 11b), with the exception of the carbon and OM relation for panne 2 of Warren Dunes which has the lowest r^2 value (Figure 11a). The average C:N ratio from all the samples recovered is 15.9 (Table 9), which lies between the C:N ratios for pastures and grasslands of 12.2 and 17 respectively (Snowdon et al., 2005) (Table 10). For a sample without carbonate, the total C obtained by the CHN analyzer, should equal the OM value multiplied by 0.4, in order to correct for non C volatization. The last plot in Figure 11a shows the relationship between carbon provided by the CHN, Carbonate free, and organic C by LOI. All the plots in Figure 11a show a positive trend between total carbon and organic matter.

4.1.1 Organic Matter Distribution

The organic matter content in the different hydrological zones of a panne, differ significantly. Using statistics, it can be seen that, for panne 6 at Indian Dunes (IDP6), the averages of the undisturbed zones are statistically different from the averages of the zones with invasives (Figure 10). This is shown by the fact that the two sigma standard deviations do not overlap.

Of the eight pannes studied, panne 1 at Sleeping Bear Dunes is the most organic rich (Table 7). The lowest organic matter content is found at panne 2 at Indiana Dunes and was 0.2%. At Indiana Dunes, the four pannes have maximum organic matter content between 10% to 17% while the lowest values from these four pannes ranges from about 0.2% to 1.4%. The two pannes at Warren Dunes have the smallest range compared to the other sites, with their values ranging from 0.5% to 6.7%.

Within a panne, the dry zone is typically, the least organic rich, while the inundated zone and the periodically inundated zone appear to have the highest organic matter content although the ranges of values do overlap (Table 8). The invasive vegetation, Phragmites australis (inundated zone) and Cattail (periodically inundated zone) from IDP6, grow in the most organic rich soil having average OM percentages of 14.6% and 16.6%, respectively. In contrast, the periodically inundated zone from SBP1, a control site, has a range from 1.2 - 32.2%, the highest OM content recorded during this study.

4.1.2 Nutrient Enrichment

Total carbon and nitrogen concentrations were obtained by using the CHN Elemental Analyzer. In order to compare concentrations of carbon and nitrogen, along the eight pannes, C content (mg/g) obtained from the analyzer was plotted against organic matter (mg/g) obtained from loss on ignition (Figure 11a) while the organic C content was plotted against nitrogen (mg/g), (Figure 11b), both obtained from the analyzer. The results show that, based on cross correlation, the pannes from each individual site behave similarly in terms of an overall positive trend of increasing OM. The carbon plots for IDP2, IDP3, IDP6 and IDP9 show lower concentrations of C against OM, compared to the plots for SBP1 and SBP2, which show the highest concentrations of C against OM, with WDP1 and WDP2 lying in between the two extremes. SBP1 has the highest concentration of carbon at 397mg/g from the periodically inundated zone. The zone growing Phragmites australis in IDP6 have values ranging from 77 - 116mg/g (inundated zone) while the zone growing Cattail from the same panne (periodically inundated zone), have values ranging from 70 - 79mg/g. Overall, a comparison of the carbon results from each panne across different locations show that panne 1 from Sleeping Bear Dunes has the highest concentrations of carbon recovered from this study. This same panne has the highest OM% recorded in this study as well, showing a relationship between high OM and high nutrients. Panne 2 from Sleeping Bear Dunes shows the second highest concentrations of total C whereas the same panne has the lowest concentrations of organic carbon recovered in this study. The pannes studied at Warren Dunes, WDP1 and WDP2, show the same relationship for total C as well as organic C plots but have the lowest organic matter concentrations recovered from this study. The four pannes studied at Indiana Dunes also have a similar trend for total C as well as the organic C results, with IDP2 and IDP6 having higher concentrations than the samples recovered from both IDP3 and IDP9. These graphs show a relationship between total C and OM(mg/g) for specific regions, with pannes from Warren Dunes showing the lowest concentrations, pannes from Sleeping Bear Dunes having the highest concentrations while the pannes from Indiana Dunes lie somewhere between. The same is true for the organic carbon concentrations between the pannes, except that panne 2 from Sleeping Bear Dunes behaves differently, having the lowest organic C concentrations recorded, supporting the statement that organic C concentrations may not be related to total C concentrations and inorganic C concentrations may contribute to this value. Figure 11a shows the importance of OM as the main carbon - bearing component of sediments in pannes, with mineral carbonate which is the total carbon minus the organic matter carbon as a very small fraction. The last plot in Figure 11a shows the carbon fraction of the sediment can range from undetectable to 200ppm (multiplied by 0.48 organic carbon conversion = 96ppm on the total C axis).

The nitrogen and organic carbon relationships are shown in Figure 11b and there is a strong positive relationship between nitrogen and organic carbon. This is a product of the incorporation of the nutrient element, nitrogen, into organic matter production.

Panne 1 from Sleeping Bear Dunes, a control site, is the panne that shows this relationship the strongest. The r^2 value of 0.92, proves this, showing a positive correlation. This positive correlation is seen for all the pannes in this study with the exception of panne 6 at Indiana Dunes which has no correlation between nitrogen and organic carbon. This is perhaps caused by a high degree of disturbance, probably resulting in accumulation of excess nutrients at the site, since it is the only panne that lies right by a roadway.

As noted in section 1.2, the area surrounding the Indiana Dunes National Lakeshore has extensive coke and coal burning industries, which is the large initial source of N to the environment. Deposition of N in the surrounding areas, comes in the form is NO_X as a component of acid rain.

Table 9 gives a breakdown of the C:N ratios encountered in this study, for the various hydrological zones of each panne. An average of 15.9 was obtained for all the C:N ratios. This is expected, based on the general C:N ratios for specific vegetation and settings (Table 10). This supports the general balance between nitrogen retention and organic matter production in the setting, with the exception of panne 6 at Indiana Dunes. This panne lies adjacent to a roadway and is directly exposed to contaminants. Panne 6 has been affected by invasive vegetation more than any other panne in this study, yet it does not stand out with unusually high nitrogen concentrations compared to other pannes at Indiana Dunes. The zones from IDP6 that have the invasive Cattails and Phragmites, do have higher nitrogen concentration than any of the other zones in pannes at Indiana Dunes, which is consistent with the fact that Cattail and Phragmites grow in nitrogen rich environments. But the pannes at the control sites at Warren Dunes and Sleeping Bear

Dunes, have the highest nitrogen concentrations recovered from this study, which cannot be explained.

4.2 Sequential Phosphorus Extractions

Phosphorus geochemistry can help define the reactivity of this nutrient element in different environments. The first fraction is referred to as occluded which is basically comprised of P bound to oxides, the major component being iron oxides (Figure 12a). Of the four pannes at Indiana Dunes, on which the Sequential Phosphorus Extraction was performed, panne 6, which is also the panne most affected by invasive vegetation in this study, had the highest amount of oxide bound Fe (2700umol/g) recovered (oxide bound Fe was determined on the extractant along with oxide - bound P). Panne 9 at Indiana Dunes, which is the second most affected panne showed a maximum value of only 165 umol/g of oxide bound Fe. The pristine panne, IDP2 and the other least affected panne, IDP3, showed oxide bound Fe values of 1400 umol/g and 700 umol/g respectively. Even though panne 6 showed oxide bound Fe at a high of 2700 umol/g, the occluded P related to this value was only found to be 1.5 umol/g. This value is similar to the other occluded P values recovered from samples obtained from other pannes as well. This data are presented in Appendix A

The main point is that no relationship exists between the oxide Fe fraction and retention of P on that fraction. Furthermore, no clear trend in the oxide content can be seen across the various settings within the pannes, indicating that iron cycling via oxide production/ dissolution plays a very small role in controlling nutrient cycling. The exception again is panne 6 from Indiana Dunes, with the highest oxide contents although little relationship exists between oxides and nutrients in this panne.

The carbonate P and the detrital P are the second and third fractions obtained from the sequential extraction respectively. They can be combined and given the name mineral P. The mineral P is the lowest in panne 2 at Indiana Dunes (27.81%) and the highest in panne 9 at Indiana Dunes (35.40%) (Figure 12e). No specific trend is observed along the four pannes studied here.

The last fraction obtained is referred to as organic P. There is a positive trend of OM with organic P for pannes 2, 3 and 6 (Figure 12b). The invasive vegetation in panne 6 has higher organic P than that of the other samples recovered.

Overall, there is no clear relation between any of the four pannes studied at Indiana Dunes and any of the four fractions of phosphorus.

Figure 12a shows the occluded P against oxide bound Fe, with no clear trend seen. Figure 12b displays the organic P against OM%, there is a positive trend for pannes 2, 3 and 6. Figure 12c, also has no clear trend seen between total P and OM%. As a group, pannes 2, 3 and 9 from Indiana Dunes, differ from panne 6. This panne has a markedly different distribution for P fractions, as it has a lack of correlation between N and C contents, which is further evidence that the expected nutrient - organic matter relationships break down for this particular panne.

Comparing the organic fraction of P, from the Sequential Extraction for pannes 2, 3, 6 and 9 (Figure 12c) at Indiana Dunes with the C and N content determined by the Elemental Analyzer for the same pannes (Figure 11b), the same trend is seen for the organic P and the total C. However, there is a difference observed between the organic P and the nitrogen content for pannes 3 and 9. Panne 3 has the third lowest correlation r^2 value for organic P and the second highest r^2 value for carbon nitrogen relationship. Panne 9 has the no trend for organic P while it has a reasonable trend for total N. Thus, the organic P results are not entirely consistent with the total N results.

4.3 Metal Distribution

The ICP - AES methods discussed in section 3.2.2 were used to obtain the concentrations of the eleven elements: Fe, Cd, Cr, Cu, Ni, Pb, Ba, Mn and Zn along with S and P (Figure 13a - 13k). Here, the metal concentrations are plotted on the Y axis with the organic matter content plotted on the X axis.

Figure 13a is a graph of Fe versus organic matter. Panne 6 at Indiana Dunes was found to have the highest Fe concentration, with the greatest values in the zone in which the Cattail and Phragmites grow (the inundated and the periodically inundated zones). Panne 9 at Indiana Dunes, has the second highest Fe concentration, with the inundated zone being the most Fe rich. This is followed by panne 2 at Indiana Dunes, having the third highest Fe concentration at Indiana Dunes (in the inundated zone) and lastly by panne 3 which has the lowest Fe concentration at the Indiana Dunes National Lakeshore. The two pannes at Warren Dunes have the lowest Fe concentrations recorded in this study, with panne 2 at Warren Dunes having more Fe concentration than panne 1. The two pannes at Sleeping Bear Dunes also have high Fe concentrations. Panne 2 from Sleeping Bear Dunes has Fe concentrations higher than panne 2, 3 and 9 from Indiana Dunes which cannot be explained. Panne 2 at Sleeping Bear Dunes has Fe concentration higher than panne 1 with the high values in panne 1 being from the periodically inundated zone and the high values in panne 2 from the inundated zone. The soil with the highest organic matter (SBP1) shows no co relation with high Fe concentration proving an insignificant relationship between the two. However, the four pannes studied at Indiana Dunes all show a positive trend of increased Fe concentration with organic matter.

Appendix A compares the % weight of Fe obtained from two different methods: Fe obtained from step 1 of the sequential phosphorus extraction (oxide - bound Fe), and total Fe obtained from the ICP - AES. In most cases, significant proportion of the total P during the Sequential Phosphorus Extraction is oxide related, with the Fe obtained from the Sequential Phosphorus Extraction being greater than the Fe obtained from the ICP - AES.

The heavy metal Cd behaves similarly with the highest Cd concentration in this study being from the zones in which invasive vegetation grow in panne 6 at Indiana Dunes. This high is followed closely by panne 9 at Indiana Dunes, leaving panne 2 and panne 3 at Indiana Dunes with the third and fourth highest Cd concentrations respectively. Considering the different sites studied, the control sites at Sleeping Bear Dunes and Warren Dunes have the second and third lowest Cd concentrations respectively. All the eight pannes show a positive trend with organic matter, with the exception of panne 3 at Indiana Dunes. This can be supported by the r^2 values (Figure 13b).

The heavy metal Cr also behaves similarly to Cd showing that the invasive vegetation growing in panne 6 at Indiana Dunes has the highest Cr concentration recorded in this study (Figure 13c). This is followed by panne 2 and panne 3 at Indiana Dunes having the second and third highest Cr concentrations and panne 9 having the lowest Cr concentration at this site. The two pannes from the control sites at Sleeping Bear Dunes have the second lowest Cr concentration, after Indiana Dunes. The two pannes at the control site at Warren Dunes, have the lowest Cr concentration recorded in this study. There is a positive trend observed with OM and Cr concentrations for all the pannes studied.

Cu also behaves in a manner similar to the previously mentioned heavy metals (Cd and Cr). Panne 6 from Indiana Dunes has the highest Cu concentrations recovered, and these were obtained from the zones which have the invasive vegetation growing in it. Pannes 2 and 9 exhibit the second and third highest Cu, respectively, with panne 9 having the lowest Cu concentration obtained from this site (Figure 13d). The control site at Sleeping Bear Dunes exhibits the second lowest Cu concentrations, after Indiana Dunes, leaving the two pannes at Warren Dunes with the lowest Cu concentrations. Also seen is the positive correlation between organic matter and Cu concentrations for pannes studied from all sites with the exception of panne 1 at Sleeping Bear Dunes.

Ni also shows similar trends to the metals discussed so far (Cd, Cr and Cu). The highest Ni concentration occurs in the zones having invasive vegetation. Maximum concentrations occur in Indiana Dunes panne 6 (Figure 13e). This is followed by panne 9 at Indiana Dunes which has the second highest Ni concentration in this study. Panne 2 from Indiana Dunes has the third highest Ni concentration recorded and panne 3 at Indiana Dunes has the lowest Ni concentration recorded from the pannes at Indiana Dunes. The concentrations from panne 3 at Indiana Dunes, are lower than the pannes at the control sites, at Sleeping Bear Dunes and Warren Dunes. Pannes 1 and 2 from Sleeping Bear Dunes have Ni concentrations higher than panne 3 at Indiana Dunes. The pannes at Warren Dunes have values that are slightly lower than those at Sleeping Bear Dunes. There is also a positive correlation between OM and Ni concentrations and this can be seen clearly in all the pannes (Figure 13e). The correlation at panne 2 at Sleeping Bear Dunes is especially strong ($r^2 = 0.87$).

The metal Pb acts a little differently than the metals that have been discussed so far. The zone within panne 6 at Indiana Dunes with invasive vegetation has the highest concentration of Pb (Figure 13f). Panne 9 at Indiana Dunes has the second highest Pb concentration. Pannes 2 and 3 at Indiana Dunes have the third and fourth highest Pb concentrations at Indiana Dunes. However, once again, panne 1 from Sleeping Bear Dunes, which is more distant from Gary, IN, an industrial city, has Pb concentrations higher than that measured from pannes 2 and 3 from Indiana Dunes. This is the same panne with the highest OM suggesting a strong affinity between OM and Pb concentration. Panne 2 at Sleeping Bear Dunes has Pb concentrations lower than panne 1 at the same site, thus indicating that the pannes are less contaminated than the pannes at Indiana Dunes. The pannes at Warren Dunes show the lowest concentrations of Pb recorded in this study. All the pannes studied show a positive correlation between OM and metal concentration. Thus, OM strongly influences concentration of all metals as predicted. OM is the dominant influence for Pb, but the results at Sleeping Bear Dunes indicate that Pb does not show the inverse correlation between distance to the source and concentration that the other metals display.

As for Ba, panne 6 from Indiana Dunes with the highest concentration of invasives, has the highest concentration of the element (Figure 13g). Panne 9 at the Indiana Dunes has the second highest Ba concentration. Next are panne 2 and panne 3 at Indiana Dunes with the third and fourth highest Ba concentrations. Panne 2 from Sleeping Bear Dunes, a control site, has Ba concentrations as high as that obtained from panne 2 and 3 at Indiana Dunes. Panne 1 from Sleeping Bear Dunes has lower Ba concentrations than panne 2 at the same site, as well as has lower values than those obtained from the pannes at Indiana Dunes. Lastly, the pannes at Warren Dunes show the lowest concentrations of Ba, with panne 2 having higher concentrations than panne 1. There also is a strong correlation between OM and Ba metal concentration, and this can be seen in every panne, showing a strong affinity for the OM and the Ba concentration.

The highest concentrations of Mn occur in the panne with the highest concentration of invasive vegetation in panne 6 at Indiana Dunes (Figure 13h). However, soil recovered from the inundated zone, in panne 6, appears to have more Mn than the soil recovered from the zones growing the cattail and phragmites (periodically inundated zone and inundated zone respectively). Panne 9 at the same site has the second highest concentration of Mn, and this is followed by pannes 2 and 3 at Indiana Dunes. The pannes studied at both control sites at Warren Dunes and Sleeping Bear Dunes, tend to behave similarly to each other. Panne 1 from both sites have similar amounts of Mn concentrations while panne 2 from both sites also show similar trends and higher Mn concentration than panne 1 from the respective sites.

Perkins et al (2000) documented that of all the metals studied, Mn behaved most uniquely, showing a very high sensitivity to the degree of inundation at each site, suggesting that Mn more likely has greater post - depositional mobility than other metals. The present study supports this assertion. In most pannes, the inundated zone appears to retain the highest amount of Mn. This would mean that the hydroperiod (the period of time during which a wetland is covered by water) has the greatest control on Mn distribution.

The last heavy metal studied is Zn (Figure 13i). The highest Zn concentration was measured in the zone with invasive vegetation in panne 6 at Indiana Dunes. This is followed by panne 9, panne 2 and panne 3 which have the second, third and fourth highest Zn concentrations respectively at Indiana Dunes. However, panne 1 at the control site at Sleeping Bear Dunes has Zn concentrations higher than those obtained from panne 2, 3 and 9 at Indiana Dunes. Panne 1 at Sleeping Bear Dunes, thus has the second highest Zn concentration measured in this study. The other control site, the pannes at Warren dunes, show the lowest Zn concentrations. Panne 1 from Sleeping Bear Dunes has the second highest concentration of Zn, but panne 2 at the same site has Zn concentrations that do not differ from concentrations in pannes at the other control site, Warren Dunes. This metal behaves similarly to Pb, Ba, Ni, etc as it displays a positive correlation with OM. This can be supported by the high r^2 values seen for all the pannes and also by panne 1 at Sleeping Bear Dunes which has the highest OM recovered in this study and the second highest Zn concentration in this study.

In terms of S (Figure 13j), panne 9 at Indiana Dunes shows the highest S concentrations recovered from this study, in the inundated zone. The zones growing the invasive vegetation in panne 6 at Indiana Dunes, show the second highest concentrations recovered in this study. Pannes 2 and 3 at Indiana Dunes have similar S concentrations, being the pannes showing the third and fourth lowest S concentrations recovered from this site, but panne 2 from Sleeping Bear Dunes, the control site, has a sample from the inundated zone, that has higher concentrations than the samples recovered from panne 2 and 3 at Indiana Dunes. The pannes at the control site, Warren Dunes, have the lowest S concentrations recovered in this study. Like the metals discussed so far, there is a strong relationship between OM and S concentrations. S is concentrated in pyrite (both mineral and bacterial), and a considerable amount comes from the burning of coal and coke, which has released significant amounts of S into the nearby environment. S is also produced from thermal plants, during paper production and metal smelting, which are all common in Gary, IN. The sequestration of various forms of reduced sulfur in sediments is a significant sink in the coupled global biogeochemical cycles of C, S and O, thereby regulating atmospheric CO_2 and O_2 concentrations on geological time scales. Organic S is thought to be the second largest pool of reduced sulfur in sediments after pyrite, but has generally been neglected in models of the C, S and O cycles (Werne, 2002).

The final element considered here is P (Figure 13k). The concentration measured in panne 1, at the control site at Sleeping Bear Dunes is the highest concentration of P measured in this study. This is the same panne having the highest OM concentration, and this indicates there is a strong correlation between P concentration and OM. The zone of invasive vegetation in panne 6 has the highest P concentration at Indiana Dunes, followed by pannes 2, 9 and 3, in that order. Both pannes at the control site Sleeping Bear Dunes have higher P concentrations than most of the pannes studied at Indiana Dunes. The lowest P concentrations occur in the pannes at Warren Dunes, a control site. Also evident is the positive correlation between OM and P concentrations, especially in panne 1 from

Sleeping Bear Dunes. Table 11 compares P values obtained from the two different methods: the sequential extraction of P versus. those obtained using the ICP - AES. In most cases, the amount of P obtained from the sequential extraction method is similar to the amount of P obtained from the ICP - AES. In some cases the sequential P amount is greater than the ICP - AES amount mainly because P is extensively extracted into four forms of P which are then added together. Overall, on calculating the percent difference in the two methods, the P obtained from the ICP - AES is greater than the P obtained from the sequential extraction of P, but overall still close.

5.0 DISCUSSION

5.1 Organic Matter and Nutrient Enrichment

In this section, distribution of organic matter is discussed. The dry/sandy zones within pannes, contain lower organic matter than the inundated and the periodically inundated zones. This is to be expected given the hydrologic regime and OM decomposition. Overall, the periodically inundated zones have organic matter marginally greater than the inundated zones in the pannes.

The organic matter values obtained in this study are much lower in general than those obtained in studies of nearby wetland and marsh environments (Dollar et al., 2001). The maximum organic matter % obtained at the surface of the pannes, in this study, was 32.2%, whereas the range of organic matter % obtained at the surface of wetlands in the Great Marsh was between 70% to 80%. Again this is expected with the hydrologic regime and OM decomposition.

Organic matter can be used to normalize metal and other data, because the amount of organic matter controls natural distribution of metals (USDA, 2001). On comparing Figures 13a - 13k, it can be seen that elevated levels of metal are found in zones with high levels of organic matter, showing that higher organic matter has an affinity for elevated metal concentrations. This is also seen in the paper by Perkins et al., (2000).

Figure 14 shows the difference between the concentrations of metals deposited at the surface and the concentrations of metals at depth at Indiana Dunes, obtained from various studies, carried out in the past (Souch et al., 2002). All of the metals graphed are more concentrated at the surface than at depth, and it is likely that this distribution has had a marked effect on the ecosystem. These graphs also show that the concentration in the pannes are higher than expected, on comparision with the Great Marsh, in relation to all the metals, Cd, Mn and Pb in particular. Figure 14 compares the results for certain heavy metals (Cd, Cr, Cu, Mn, Pb, and Zn) obtained from this study, to other studies conducted in the same area. For some of the above metals (Cd, Mn and Pb) the concentrations recovered from this study were higher than the concentrations recovered from previous studies, considering metal concentrations at the surface and at depth. However, concentrations of Mn are comparatively higher than concentrations from previous studies, going back to the post - depositional mobility of Mn factor talked about in section 1.2 and 4.3. The metals Cr and Cu show similar trends with some of the data recovered from this study having lower concentrations than the studies they are being compared to (at surface and at depth). Zn concentrations recovered from this study stand out, with zones growing the invasive species from panne 6 at Indiana Dunes having higher Zn concentrations than the majority of the concentrations from this study, but all the concentrations from this study are significantly lower than the concentrations recovered from previous studies, that they are being compared to.

Panne 6 at the Indiana Dunes which is the only panne where the invasive vegetation has had the strongest negative impact (the panne where invasive species are the most abundant) also shows up as having the highest metal concentration compared to other pannes and sites in most cases, supporting the conclusion that invasive vegetation can tolerate and retain higher metal concentrations and can prevail and thrive successfully.

Disturbance of the pannes seems to be reflected in unique organic matter to metal ratios and nutrient ratios (high organic matter tends to have high metal concentration).

This can be seen by comparing Figures 13a - 13k, which show the organic matter content against metal concentrations, and Figure 11a, which shows the carbon content against organic matter content. Panne 6 at Indiana Dunes has an overall geochemistry that is far different than the pristine pannes considered in this study. This unique relationship is reflected in the graphs for panne 6 at Indiana Dunes. Internal studies conducted by the park service on the vegetation in pannes at Indiana Dunes, have shown that panne 6 is the only panne that has been affected to such a large extent, with about 50% of the native vegetation being replaced by invasive vegetation. (Dan Mason, personal communication). When comparing all the graphs for panne 6 from Indiana Dunes, with the graphs for all the other pannes considered in this study, the negative relationship for panne 6 from Indiana Dunes, stands out.

5.2 Nutrient Distribution

Nutrient enrichment is obvious in this setting, considering carbon, nitrogen and phosphorus, of which the pannes have elevated concentrations. As discussed before, organic matter tends to hold on to nutrients. This can be seen in Figure 11a and 11b, where carbon is graphed against organic matter and carbon against nitrogen respectively. The enriched nutrients influence panne ecosystems.

The nutrient distribution is strongly controlled by the overall organic matter. The C:N ratios obtained are typical of other soils, but they are found to have a very wide range, reflecting the range of sandy to loamy soils in the panne (Snowdon et al., 2005). There is a strong positive relationship between high levels of organic matter, high concentration of nutrients, and abundance of invasive plants at one particular site, panne 6 at Indiana Dunes, but nutrients at IDNL are not much different from those in more distant sites, the control sites, Sleeping Bear Dunes and Warren Dunes. This is reflected in the nitrogen deposition pattern in Figure 11b. Overall, there is definitely nutrient enrichment at the pannes studied, considering concentrations of nitrogen, phosphorus and carbon, but, there is not much of a difference across the pannes at Indiana Dunes and the control sites, proving the fact that nutrient enrichment is probably not a reason for the shift in vegetation from native to invasive.

Figure 12d shows results for the phosphorus extractions from this study compared to phosphorus extraction results from other studies done in different environments: British Columbia Lakes, Laguna Zoncho, Costa Rica, Jackson Pond, Western Appalachian Plateau, and Dry Lake, San Bernardino Mountains, CA. In Figure 12d, the lake sites varied geographically and physically with British Columbia, Laguna Zoncho and Jackson Pond being permanently inundated small lakes, whereas Dry Lake was periodically inundated and likely is the most similar to the panne site here, although much bigger.

Research has identified that climate, especially rainfall and temperature, are the most important factors affecting soil C and N values. P content of the soil parent material, degree of weathering, and topographical influences are also important. Vegetation cover influences both the amount and quality (C:N ratio) of soil organic matter. Forests with Eucalypt vegetation generally tend to have high (21 - 33) C:N ratios in surface soils whereas ecosystems dominated by other genera tend to have lower ratios. Certain extreme environmental conditions will produce extreme C:N ratios. Saturated anaerobic conditions, cold temperatures, and strongly leaching conditions can result in very high C:N ratios, while high temperatures and low rainfall can produce very low C:N ratios. (Snowdon et al., 2005).

5.3 Metal Distribution

There is a strong variation in metal content between the sites studied for most of the metals considered in this study. Principally, the pannes near the primary sources of metal deposition at INDU have a much higher metal content than the pannes studied at Warren Dunes and Sleeping Bear Dunes, the control sites. The pannes studied at Indiana Dunes, seem to have the capability of retaining heavy metals. Also, the highest metal contents recovered in this study are in the heavily disturbed and invaded, panne 6 at Indiana Dunes, which also has the highest organic matter.

Thus, it is possible that the high metal content present in the pannes at Indiana Dunes is controlling the invasion of panne environment or it may be linked to soil and hydrological conditions that result in high organic matter regions within a panne.

A number of the elements considered in this study behave similarly (Figure 13a - 13k). There is a strong positive correlation between the different elements and organic matter. Panne 1 from Warren Dunes and panne 2 from Sleeping Bear Dunes, behave similarly for all the elements studied. The concentration, for all the eleven metals and elements studied, increases with increasing organic matter, with the exception of the metal Fe. Panne 1 from Sleeping Bear Dunes also behaves similarly, but the metal Cu acts like Fe showing no definite trend. Pannes 2 and 3 from Indiana Dunes show a very strong trend of increasing metal concentration with increasing organic matter for all 11 elements and metals. The metal Pb stands out for panne 2 from Warren Dunes along with the metals Ni, Cd and Fe for panne 3 from Indiana Dunes with a very weak trend. Lastly, the element P stands out for panne 9 from Indian Dunes, with a very weak relationship between concentration and organic matter.

6.0 CONCLUSION

The pannes at INDU, Warren Dunes and Sleeping Bear Dunes are very rare features, and have not been studied intensively. Pannes are not known to occur anywhere else in the United States. Several studies have been conducted on presence of metals in wetland sediments at the Indiana Dunes, in the adjacent areas, but none in ecosystems similar to pannes.

Overall, the results obtained from this study show that there are differences in heavy metal content and nutrient levels among the pannes studied at the Indiana Dunes. It is also clear that organic matter content of the sediments supports these differences. The results also show how important organic matter is in terms of retaining metals. There is high retention of heavy metals and nutrients in panne 1 at Sleeping Bear Dunes which also has the highest organic matter measured in this study. Very little difference exists from site to site, if metal retention and organic matter are considered and compared. This result, the strong correlation between organic matter and heavy metals studied, is found despite the closeness of Indiana Dunes to Gary, IN, a highly industrialized city, which stresses on the role organic matter plays in the retention of heavy metals and the elements studied.

This study has proven that the most disturbed pannes have the most distinctive geochemical signature, the most disturbed pannes being the pannes from Indiana Dunes, IDP6, IDP9, IDP3 and IDP2, in that order. However, this study was not able to establish the cause and effect relationship. The distribution of the heavy metals and nutrient levels within a panne, show a spatial distribution, with emphasis on the organic matter content.

The combination of high levels of organic matter, high concentrations of nutrients, and high concentration of metals are a “risk factor” that will aid future invasion of pannes by invasive species, because these species tolerate this combination better than native species.

Overall, there are similar differences among the pannes at INDU, when heavy metals and nutrient enrichment are compared. It can also be seen that organic matter plays a very strong role in these differences. The pannes studied at Warrren Dunes, a control site, had the lowest concentrations for every single element studied, however, the pannes studied at Sleeping Bear Dunes (where pollution is less), another control site, had lower concentrations for most of the elements studied compared to those at Indiana Dunes (where pollution is more), in most cases, but not significantly lower.

The periodically inundated zone within a panne, tends to hold on to more heavy metals and nutrients than the rest of the panne (inundated zone, dry zone), showing the presence of a spatial component across a panne. A clear relationship can be seen between distribution of invasive species, heavy metals and organic matter. However, there is no clear relationship between nutrients and distribution of invasive species. Invasive vegetation could possibly be able to tolerate this combination of high organic matter, high metals and high nutrients and tend to prevail and flourish.

TABLES

Table 1: Sources of heavy metals and elements studied.

Elements	Sources
C	produced by *combustion of fossil fuels* (wood, natural gas, coal and oil)
N	produced by *combustion of fossil fuels* (coal), manufacture of fertilizer
P	Found in fertilizers and sewage, detergents, used by industries to make other chemicals.
Fe	used in metallurgy, refining of iron ores, release of industrial wastes
Cd	manufacture of batteries, plastics, ceramics, glasses, paints, enamels, PVC, *combustion of fossil fuels*.
Cr	produced by *combustion processes*, metallurgical industries, refractory industries, component of stainless steel and metal alloys, electroplating industries.
Cu	stack emissions of *coal burning power plants*, copper processing operations
Ni	manufacture of stainless steel, alloys, parts of jet engines, used in land based combustion turbines in electric power stations, batteries, manufacture of chemicals, foundry products and plating.
Pb	*combustion of fossil fuel*, smelters, car battery plants, power plants, common industrial source.
Ba	used by oil and gas industry, manufacture of paint, bricks, tiles, glass, rubber, lead alloys, batteries, soap, linoleum
Zn	*combustion of fossil fuel*, steel processing, galvanizing steel, producing alloys, metal manufacturing industries and coal ash from electrical utilities.
Mn	*combustion of fossil fuels*, iron and steel producing plants, power plants, coke ovens, dust from mining.
S	*combustion of fossil fuel*, thermal plants, paper production and metal smelting, petroleum products, combustion of fuel oils and coal.

Table 2: List of prominent industries in the 57.2sq miles (148 sq km) area of Gary, Indiana. (Source: *http://www.in.gov/idem/air/emissionsdata/* last accessed on May 15th, 2005).

US Steel (16 miles from IDNL)
Bethlehem Steel (2.8 miles from IDNL)
Inland Steel Corporation (23 miles from IDNL, sixth largest in nation)
American Sheet and Tube Company (25 miles from IDNL)
Worthington Steel (5 miles from IDNL)
US Midwest Steel (5.13 miles from IDNL)
Munster Steel (26.08 miles from IDNL)
Industrial Steel Construction, Inc (18 miles from IDNL)
ISPAT Steel (23.9 miles from IDNL)
LaSalle Steel Company (24.5 miles from IDNL)
Jupiter Aluminum Corporation (23.8 miles from IDNL)
Gary Coal Processing (15.8 miles from IDNL)
Marathon Ashland Pipeline (28.2 miles from IDNL)
BP Chemical Company (27.19 miles from IDNL)
Cargill, Inc (5.7 miles from IDNL)
Carmeuse Lime Incorporated (20.06 miles from IDNL)
Citgo Petroleum (22.37 miles from IDNL)
Ironside Energy (23.5 miles from IDNL)
Praxair (2 miles from IDNL)
Heritage Slag Products, LLC (23.9 miles from IDNL)
Shell Oil Products (23.8 miles from IDNL)
Central Illnois Steel Co (9 miles from IDNL)

Table 3: Typical detection limits and reproducibility of the ICP – AES. Iron is represented in wt% while the other elements are represented in ppm.

Element	Typical Detection limit* (ppm)	Typical Analytical Reproducibility ** (%)
Zn	1.3	1.1
Mn	0.4	1.3
Ba	0.1	1.4
Fe	0.27 (wt %)	1.5
Cd	0.3	3.8
Cu	0.7	4.2
P	10.8	4.3
Cr	1.5	4.8
Pb	8.4	6.1
Ni	2.7	6.4
S	7.8	8.9

*Three times the standard deviation of blank samples.
** Average standard deviation of all samples.

Table 4: Extraction Steps for Sequential Phosphorus Extraction. (Source: Latimer and Filippelli, 2001).

Step	Reagents	P component isolated
Oxide - associated	10mL CDB solution (6h) (0.22 M Na citrate, 1M $NaHCO_3$, 0.13 M Na - dithionite), 10mL of 1 M $MgCl_2$ (2h), 10mL H_2O (2h)	Adsorbed and reducible or reactive Fe - bound
Authigenic	10mL of 1M Na - acetate buffered to pH 4 w/acetic acid, 10mL of 1M $MgCl_2$ (2h) - twice, 10mL H_20(2h)	Carbonate fluorapatite (CFA), biogenic hydroxy apatite, and $CaCO_3$ - bound P
Detrital	10mL of 1M HCl (16h)	Detrital P
Organic	1mL 50% (w/v) $Mg(NO_3)_2$, dry in low oven, ash at 550 degrees C (2h), add 10mL of 1M HCl	Organic P

Table 5: Percent error for the CHN Elemental Analyzer.

Elements	C (%)	H (%)	N (%)
ID P2	1.35	7.42	0.96
ID P3	1.36	4.68	1.92
ID P6	0.20	4.36	1.99
ID P9	0.29	1.91	0.32
SB P1	0.01	2.11	1.01
SB P2	1.47	5.71	0.98
WD 1&2	0.43	2.21	1.17

*The formula used to calculate the % error was (measured value – actual value/ actual value)*100

Table 6: Detection limit for the CHN Elemental Analyzer.

Elements	N (mg)	C (mg)	H (mg)
Detection Limits**	0.000	0.002	0.001

*Three times the standard deviation of blank samples

Table 7: Organic Matter Percent (OM%) for all eight pannes in this study including the highest, lowest and average OM%, determined by loss on ignition for all samples within a panne. Results are presented in percent.

Pannes	No of samples	Highest OM%	Lowest OM%	Average OM%
ID P2	24	16.2	0.2	4.8
ID P3	24	10.5	1.1	4.4
ID P6	40	17.0	0.7	7.0
ID P9	38	11.2	1.4	4.5
SB P1	20	32.2	0.9	6.9
SB P2	18	12.0	0.4	2.0
WD P1	12	6.2	0.5	2.4
WD P2	9	6.7	2.1	5.0

Table 8: Ranges of OM% and average OM% from different hydrological zones within a panne.

Pannes	Inundated Zone		Periodically Inundated Zone		Dry Zone	
	Range	**Average**	**Range**	**Average**	**Range**	**Average**
ID P2	2 - 8.3	4.8	16.2		0.2 - 9.9	3.7
ID P3	1.3 - 7.3	4.1	5.5 - 10.1	7.8	1 - 10.4	3.9
ID P6	0.6 - 7.1	5.4	1.2 - 10.2	4.5	0.7 - 7.2	4.2
IDP6 (Invasive Zone)	10.4 - 15.6 {P}	14.6	16.2 - 17 {C}	16.6		
ID P9	1.9 - 11.2	5.9	2.4 - 4.1	3.1	1.3 - 3.8	2.5
SB P1	1.6 - 4.1	2.8	1.2 - 32.2	9.9	0.8 - 3.7	2.2
SB P2	0.7 - 11.9	2.4	0.4 - 4.1	1.5		
WD P1	1.1 - 2.4	1.7	1.6 - 5.7	3.3	0.5	
WD P2	4.1 - 4.3	4.2	2 - 6.7	5.2		

{P} = Phragmites, {C} = Cattail.

Table 9: C:N ratios for all the pannes in this study, divided by different hydrological zones encountered.

Zones	WD P1	WD P2	SB P1	SB P2	ID P2	ID P3	ID P6	ID P9
Inundated Zone	28.2	6.4	2.8	2.5	10.6	37.8	14.0	8.0
	7.9	6.9	1.4	2.2	9.3	35.2	17.1	11.5
	2.5			1.7	25.0	16.6	10.8	9.0
	8.1			1.5	22.4	21.4	10.6	10.9
	8.3			3.4	16.3	34.3	9.5	10.1
	7.2			2.9	34.4	14.0	10.9	8.3
				1.5	28.0	16.3	12.2	10.7
				1.7	20.3	18.9	7.5	12.4
				8.2		15.4	12.1	9.6
						15.2		10.0
						22.4		13.8
						31.6		11.8
						23.1		15.1
								12.3
								11.7
								10.4
								12.5
								17.0
								15.9
								14.5
								16.0
Average	10.4	6.6	2.8	2.8	20.8	23.2	11.6	12.0
Std Dev	8.2	0.2	0.7	2.0	8.0	8.2	2.6	2.5

Zones	WD P1	WD P2	SB P1	SB P2	ID P2	ID P3	ID P6	ID P9
Periodically Inundated Zone	6.5	6.5	1.6	2.6	7.9	27.4	8.2	10.1
	6.4	6.2	1.6	2.3		14.6	9.4	16.0
	8.1	7.0	1.4	2.2			20.3	11.6
	13.0	7.2	1.2	6.6			13.1	10.7
		4.3	4.0	2.9			15.6	11.9
		13.0	3.2	6.6			13.7	11.0
			6.2	2.5			14.0	7.3
			6.0				11.0	9.8
			6.7				50.8	6.3
			5.0				24.3	8.3
							2.7	
Average	8.5	7.4	3.7	3.7	7.9	21.0	16.7	10.3
Std Dev	3.1	2.9	2.2	2.0		9.1	12.7	2.7

Zones	WD P1	WD P2	SB P1	SB P2	ID P2	ID P3	ID P6	ID P9
Dry Zone	37.9		2.5		51.0	15.3	8.3	16.7
	41.3		1.9		13.0	24.3	7.6	13.7
			1.5		13.9	30.1	11.8	12.1
			3.9		18.7	18.1	11.9	12.4
			1.7		11.8	125.5	20.3	11.9
			3.5		18.2	326.6	23.9	15.4
					12.0		15.5	8.9
					38.2		12.5	
					9.7		22.7	
Average	39.6		2.5		20.7	90.0	14.9	13.0
Std dev	1.7		0.9		13.4	112.5	5.7	2.3

Table 9 (continued):

Zones	WD P1	WD P2	SB P1	SB P2	ID P2	ID P3	ID P6	ID P9
Inundated Zone - Phragmites							13.4	
							13.7	
							15.9	
							18.6	
							17.5	
							16.4	
Average							15.9	
Std dev							1.9	
Periodically Inundated Zone - Cattail							15.8	
							16.7	
Average							16.2	
Std dev							0.5	

Table 10: C:N ratios in surface soil layers for various forest ecosystems. (Source: National Carbon Accounting System – technical report no. 45).

Ecosystem	C:N ratio
Sub - alpine forest	29.6
Mixed forest	27.9
Rainforest	24.6
Grassland	17.0
Pasture	12.2

Table 11: P obtained from ICP - AES compared to that from Sequential P Extractions, graphically represented in Figure 11c. For most samples, P obtained from the sequential P analysis is lower than that obtained from the ICP - AES, with the exception of a few samples.

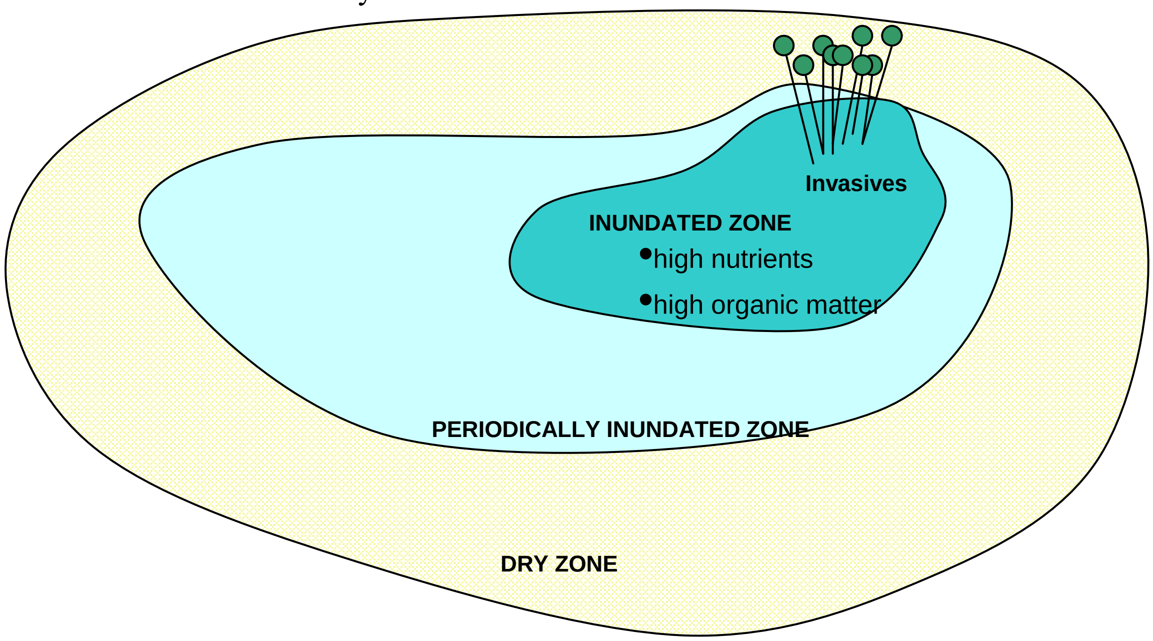
Sample ID	P obtained from Sequential P Extraction (ppm)	P obtained from ICP - AES (ppm)
ID - P2 - 10	135.11	105.71
ID - P2 - 12	129.76	112.93
ID - P2 - 14	101.54	151.27
ID - P2 - 20	138.97	168.66
ID - P2 - 07	226.81	236.20
ID - P2 - 17	110.04	108.03
ID - P2 - 02	48.43	92.24
ID - P2 - 03	393.70	99.78
ID - P2 - 06	48.60	80.78
ID - P2 - 08	87.55	76.11
ID - P2 - 18	1.14	100.25
ID - P2 - 21	109.51	156.57
ID - P3 - 16	59.38	170.90
ID - P3 - 17	79.81	58.10
ID - P3 - 17X	91.06	70.26
ID - P3 - 17Y	76.41	85.25
ID - P3 - 01	119.30	141.13
ID - P3 - 04	36.25	85.03
ID - P3 - 06	102.44	157.45
ID - P3 - 09	125	115.79
ID - P3 - 10	159.73	148.27
ID - P3 - 11	170.16	113.60
ID - P3 - 08	123.14	114.35
ID - P3 - 15	21.53	90.67

Table 11 (continued):

Sample ID	P obtained from Sequential P Extraction (ppm)	P obtained from ICP - AES (ppm)
ID - P6 - 25	99.10	146.21
ID - P6 - 28	118.05	109.53
ID - P6 - 22	125.16	133.41
ID - P6 - 23	98.11	134.03
ID - P6 - 23A	102.18	155.60
ID - P6 - 24	125.34	144.05
ID - P6 - 29	237.83	424.67
ID - P6 - 30	93.11	332.12
ID - P6 - 08	118.18	92.69
ID - P6 - 12	216.71	217.55
ID - P6 - 14	8.88	179.39
ID - P6 - 31	129.29	222.17
ID - P6 - 32	159.46	255.77
ID - P6 - 33	99.65	301.50
ID - P6 - 33A	146.41	260.81
ID - P6 - 34	105.47	257.20
ID - P6 - 18	111.29	185.26
ID - P6 - 03	133.31	251.96
ID - P6 - 05	68.45	140.66
ID - P9 - 3A	187.64	191.42
ID - P9 - 09A	114.08	98.29
ID - P9 - 10	94.86	89.22
ID - P9 - 15	130.38	121.44
ID - P9 - 03	73.81	110.58
ID - P9 - 08	44.61	94.42
ID - P9 - 16	121.24	120.21
ID - P9 - 20	111.87	122.26
ID - P9 - 23	113.29	95.69
ID - P9 - 22	176.78	189.69
ID - P9 - 32	132.97	145.76
ID - P9 - 25	143.63	137.73
ID - P9 - 30	50.70	92.16
ID - P9 - 28	155.28	102.77

FIGURES

Figure 1: A schematic diagram of a panne studied at INDU, showing the hydrological zones identified for the study.



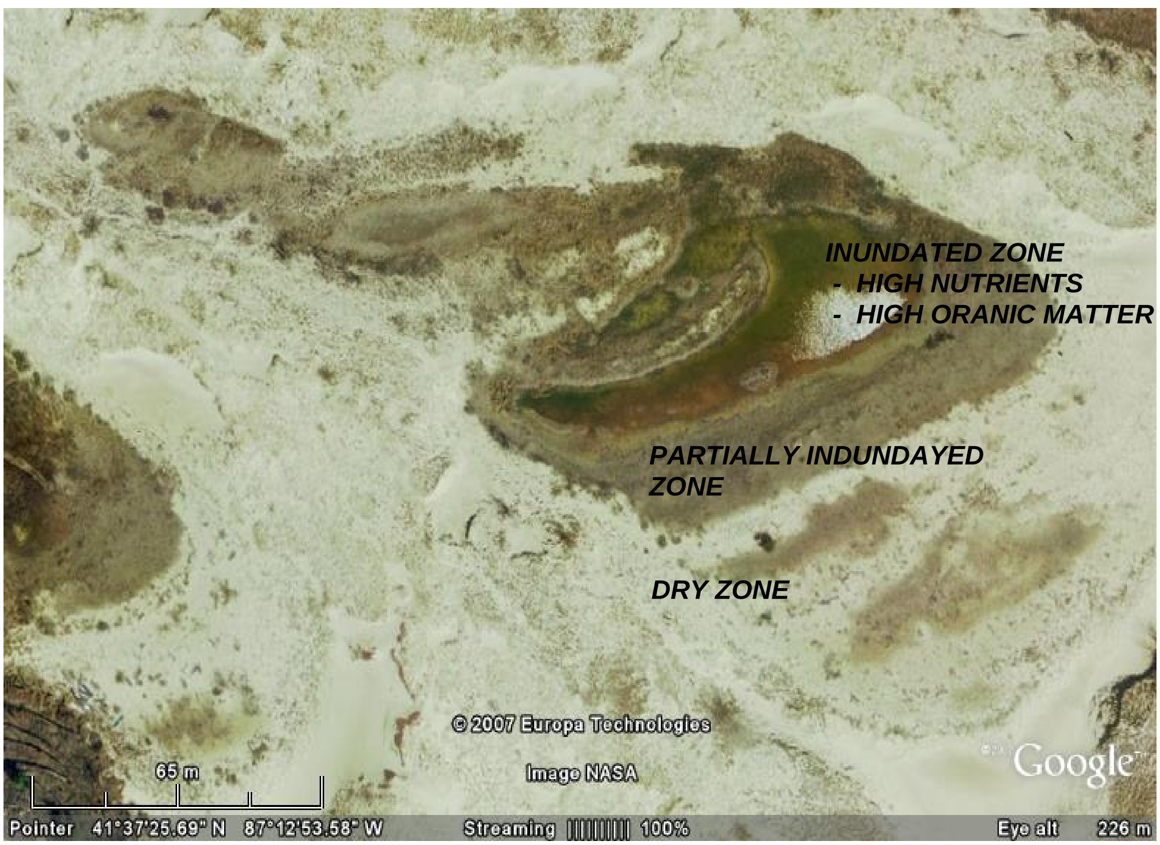


Figure 2: Hydrograph showing the fluctuating levels of Lake Michigan from 1860 - 2000. Lake levels are reported in meters. (177.4 meters = 582.02 feet) (Source: http://www.glerl.noaa.gov/data/now/wlevels/lowlevels/plot/Michigan - Huron.gif).

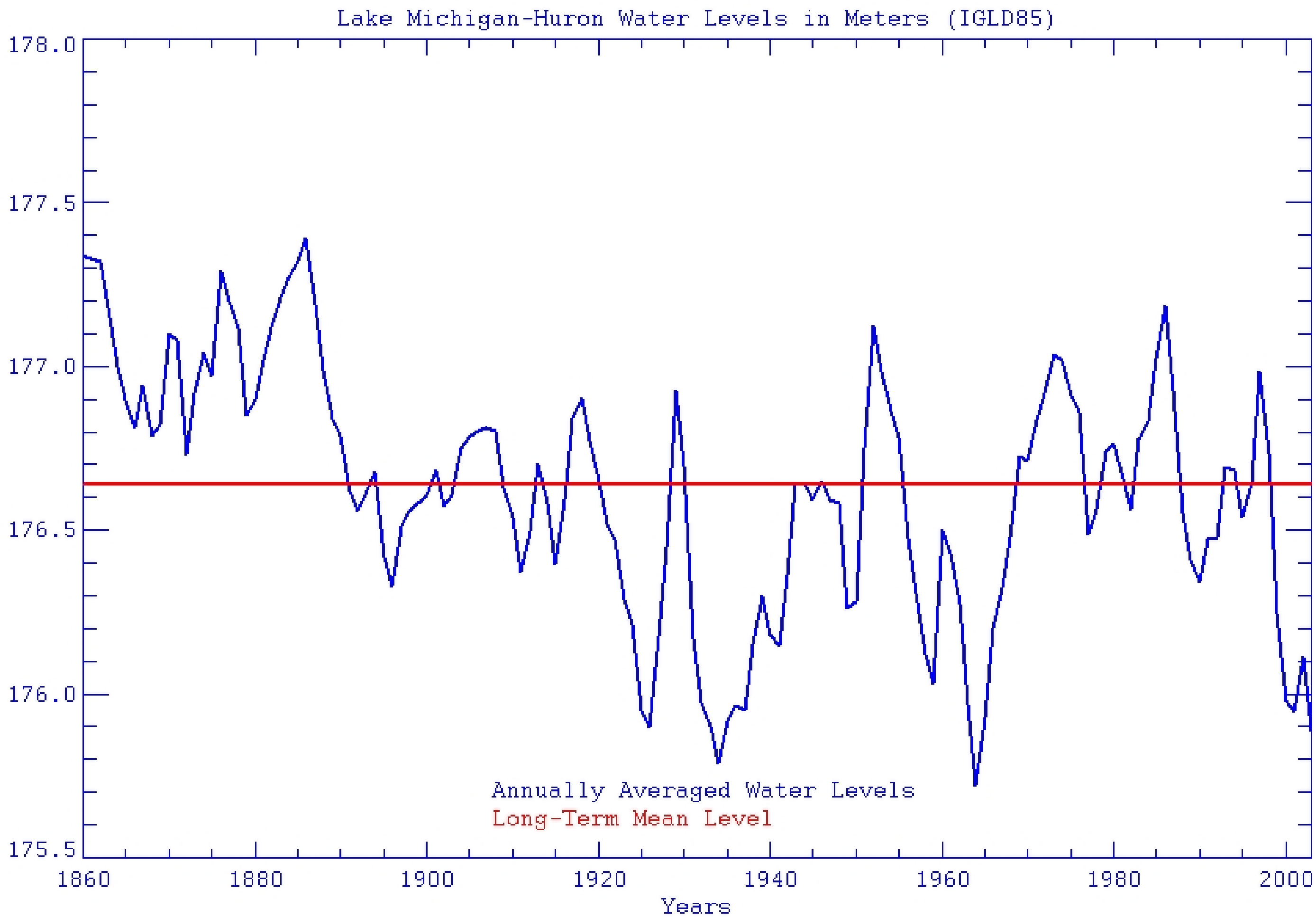


Figure 3: Isopleth showing the inorganic Nitrogen wet deposition in the United States in 2003.

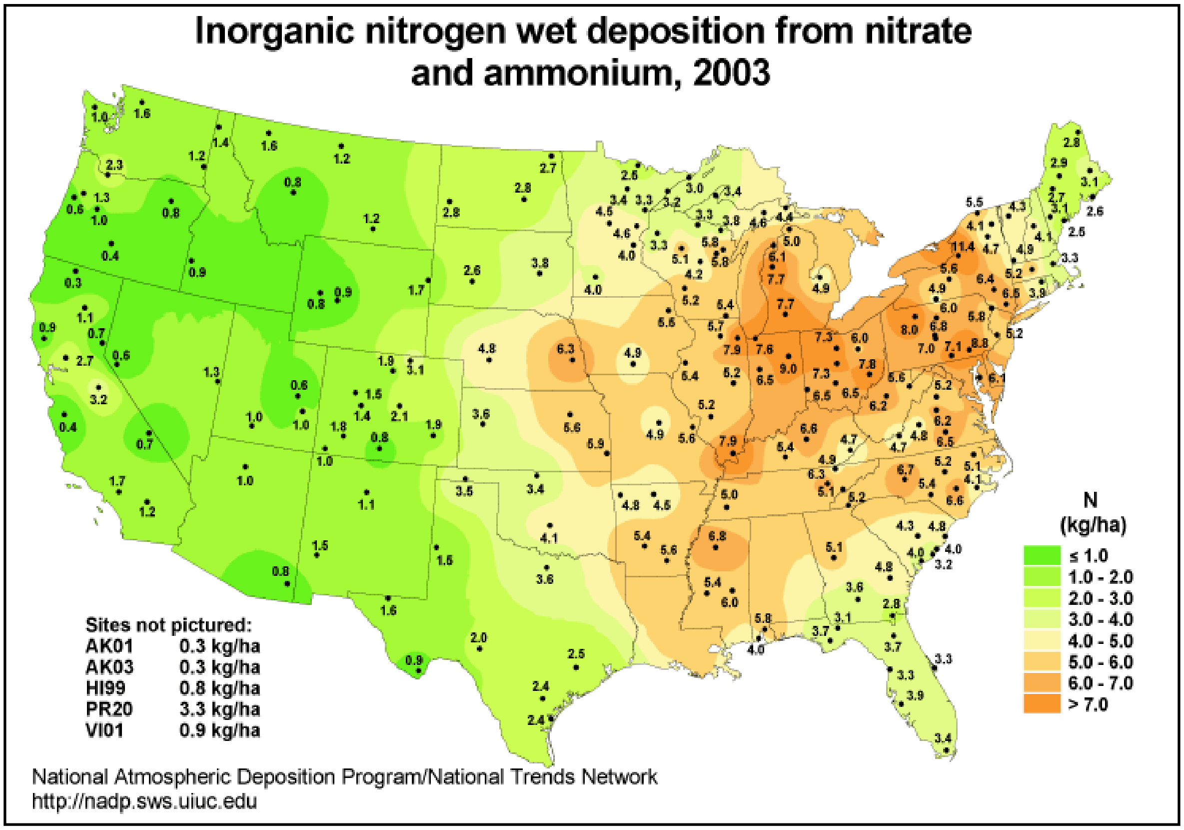


Figure 4: The three sites studied and their relative location to each other. Source: http://www.lib.utexas.edu/maps/us_2001/michigan_ref_2001.jpg.

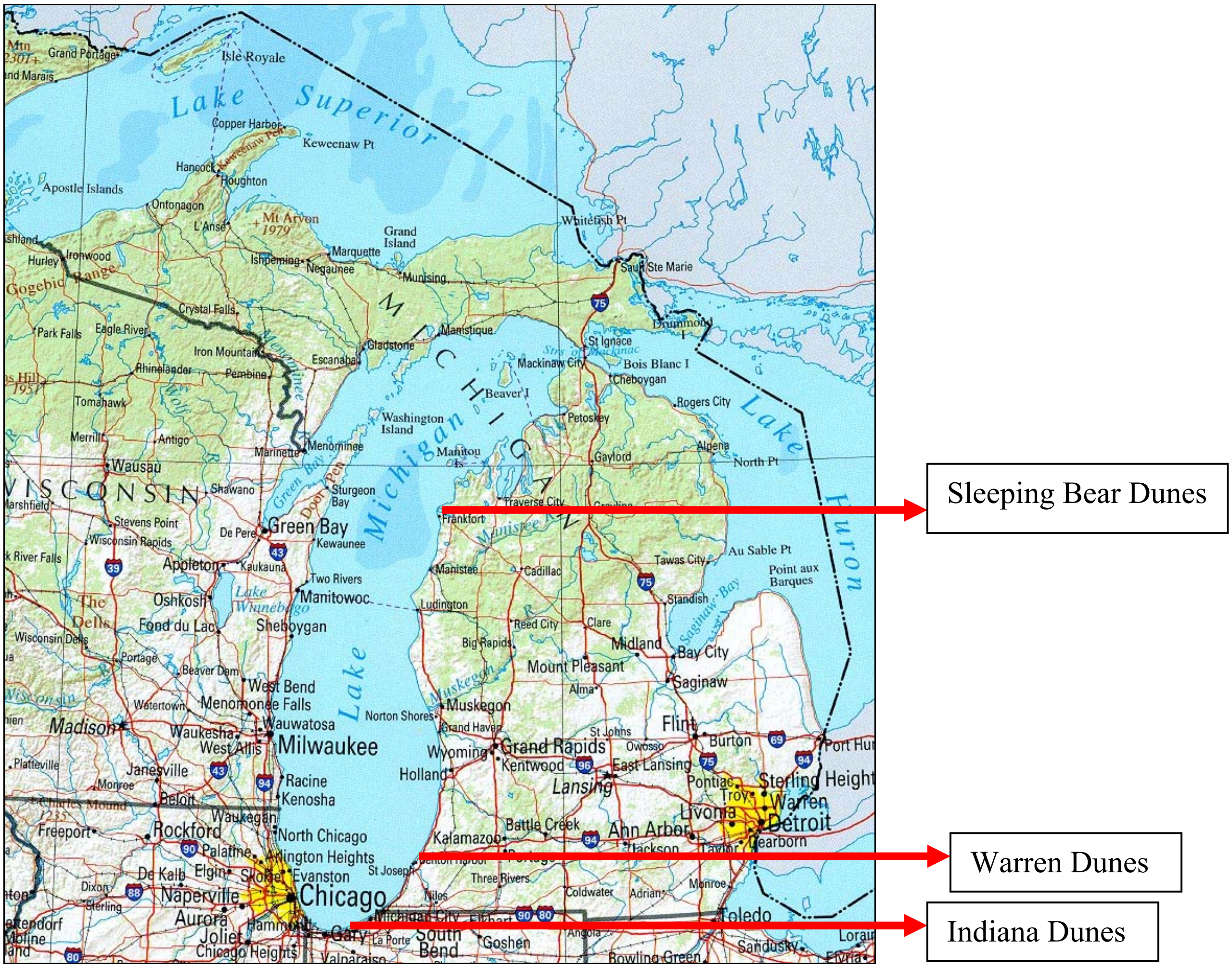


Figure 5a: Location of Indiana Dunes National Lakeshore. (Ogden Dunes at West Beach). Source: http://www.indianaoutfitters.com/Maps/Dunes/west.htm.

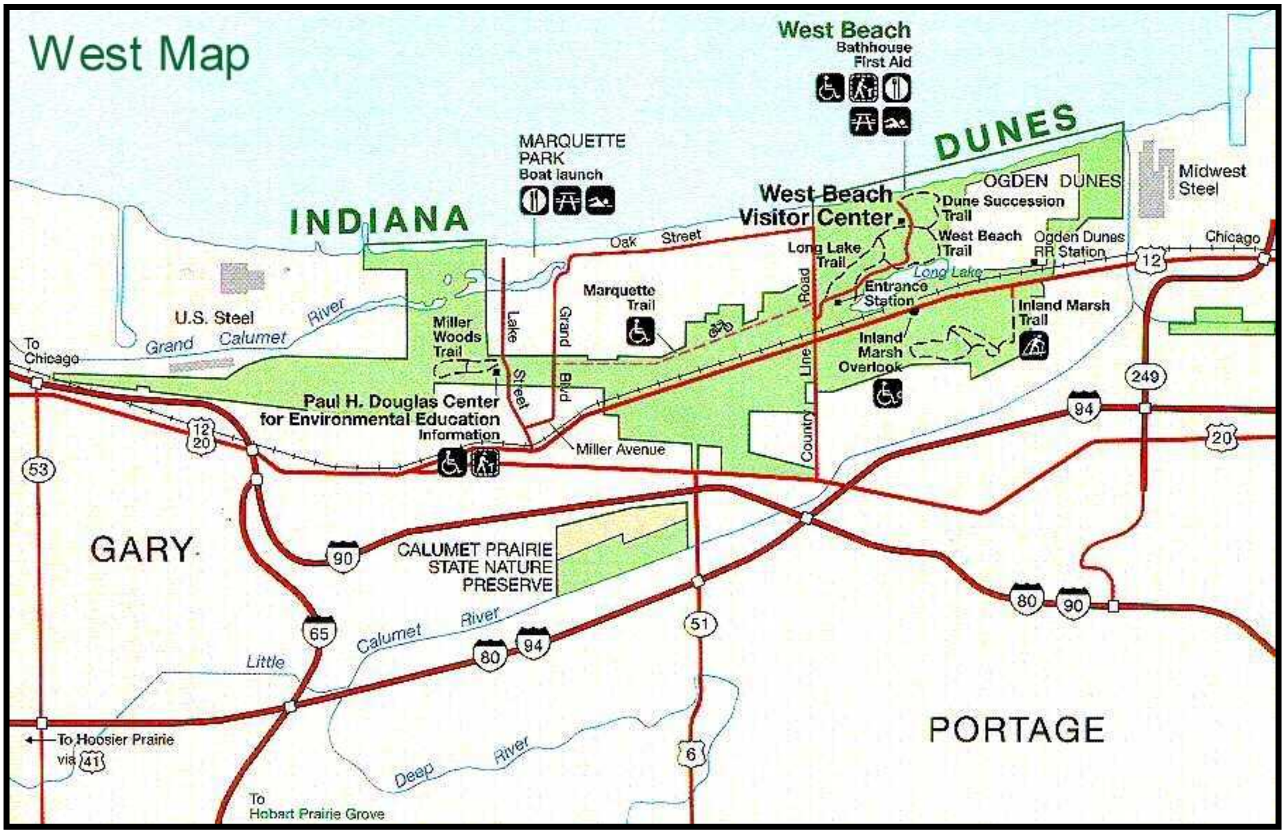


Figure 5b: INDU lying in the downwind direction of prevailing westerly winds from Gary, IN.

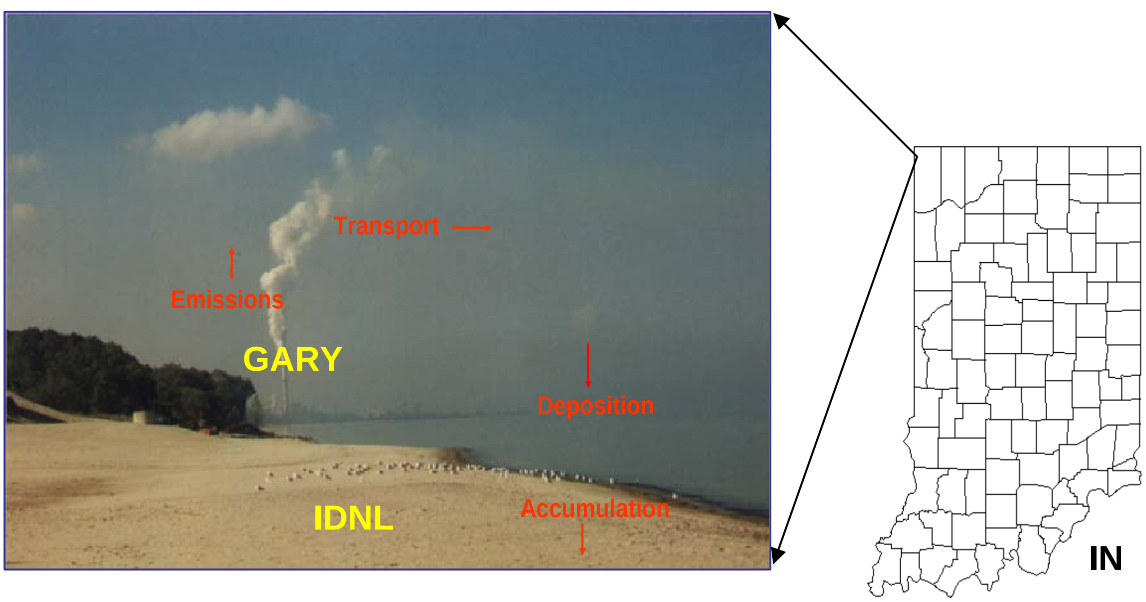


Figure 6: Map showing the ten pannes at Indiana Dunes National Lakeshore (INDU). (Aerial Photograph purchased from USGS).

Figure 7a: Two pannes studied at Sleeping Bear Dunes. Photograph taken in August 2004.

Figure 7b: Aerial photograph of the two pannes studied at Sleeping Bear Dunes showing the sample locations. (Aerial photograph purchased from the USGS).

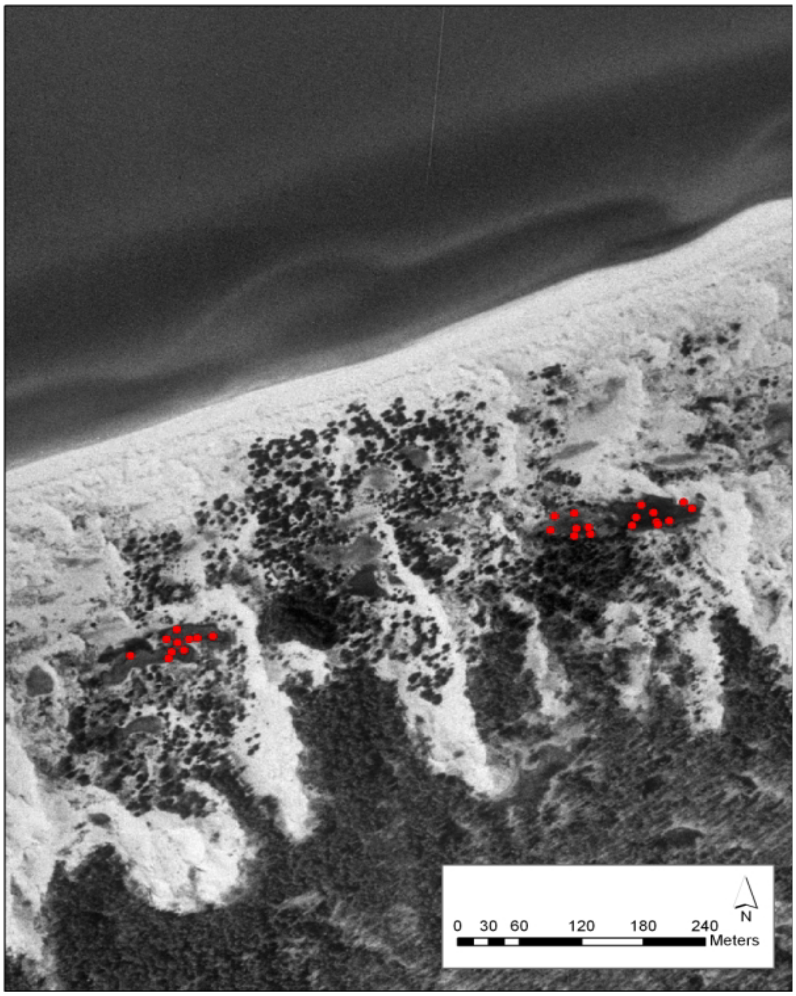


Figure 8a: Two pannes studied at Warren Dunes. Photograph taken in June 2004.

Figure 8b: Aerial photograph of the two pannes studied at Warren Dunes showing the sample locations. (Aerial photograph purchased from the USGS).

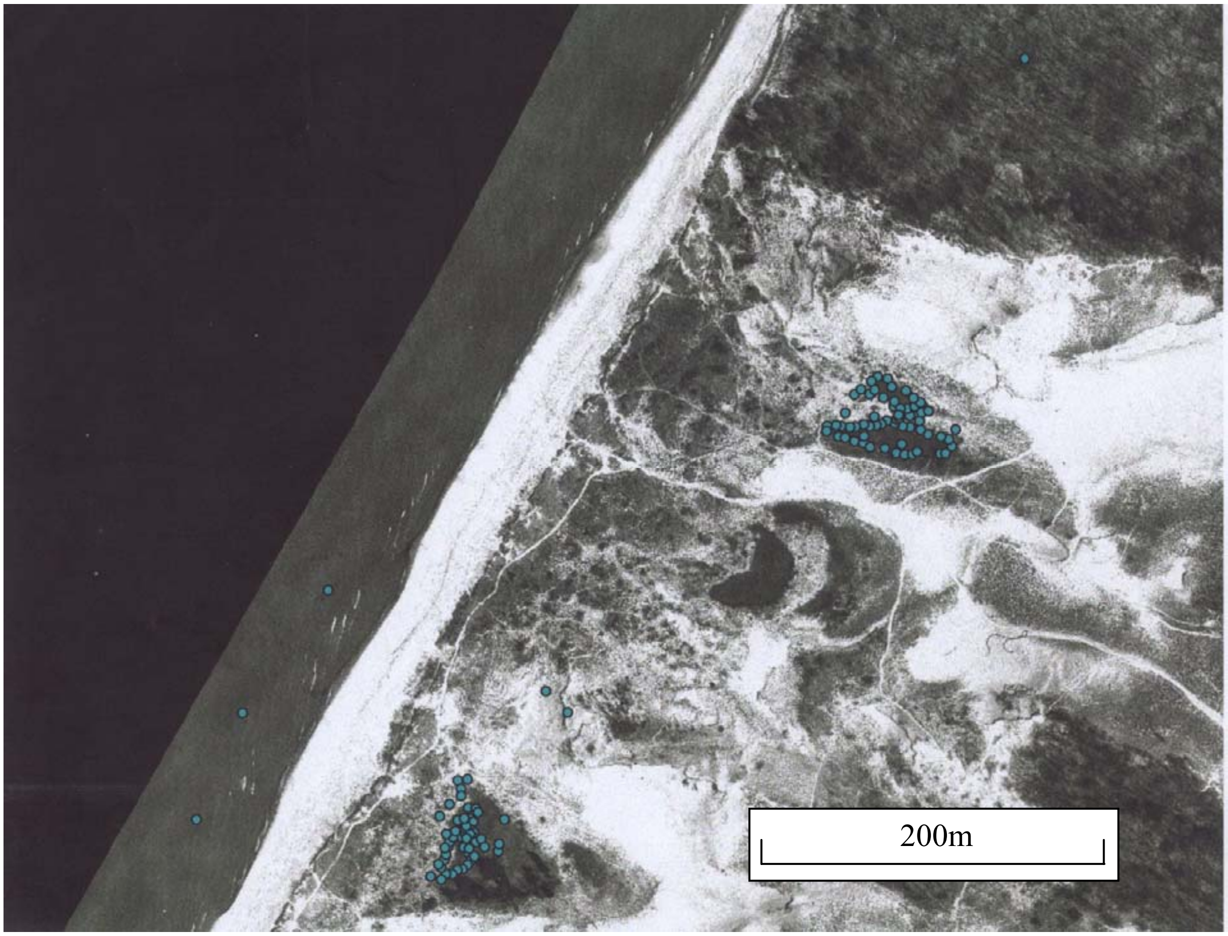


Figure 9: Using a sterile seven inch sample scoop for sampling sediment at a panne at Indiana Dunes.

Figure 10: Organic Matter percent variations in different zones in panne 6 at Indiana Dunes (IDP6).

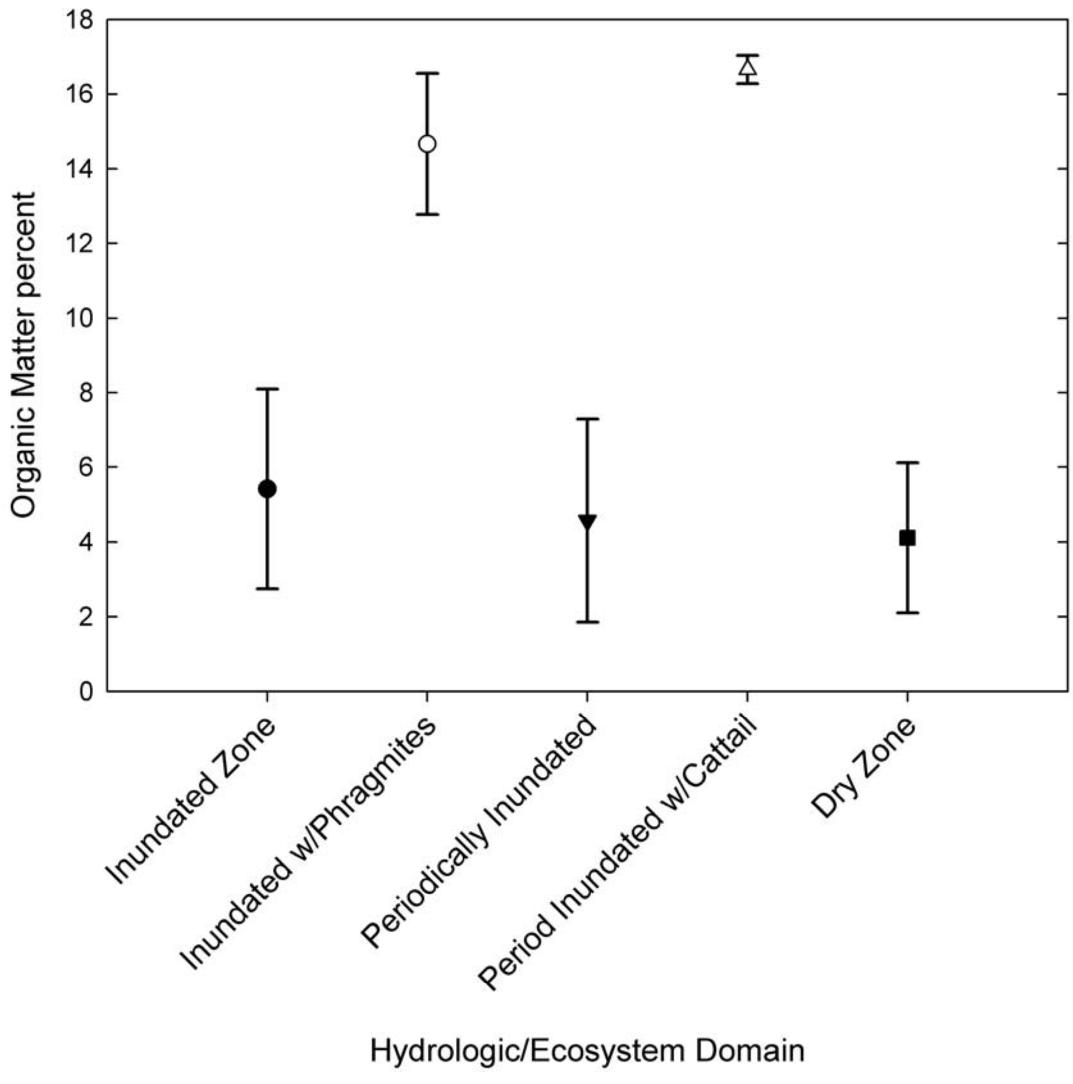


Figure 11a: Scatter plots of total Carbon content (mg/g), obtained by CHN analyzer, against OM (mg/g), and obtained by LOI, for all eight pannes in this study.

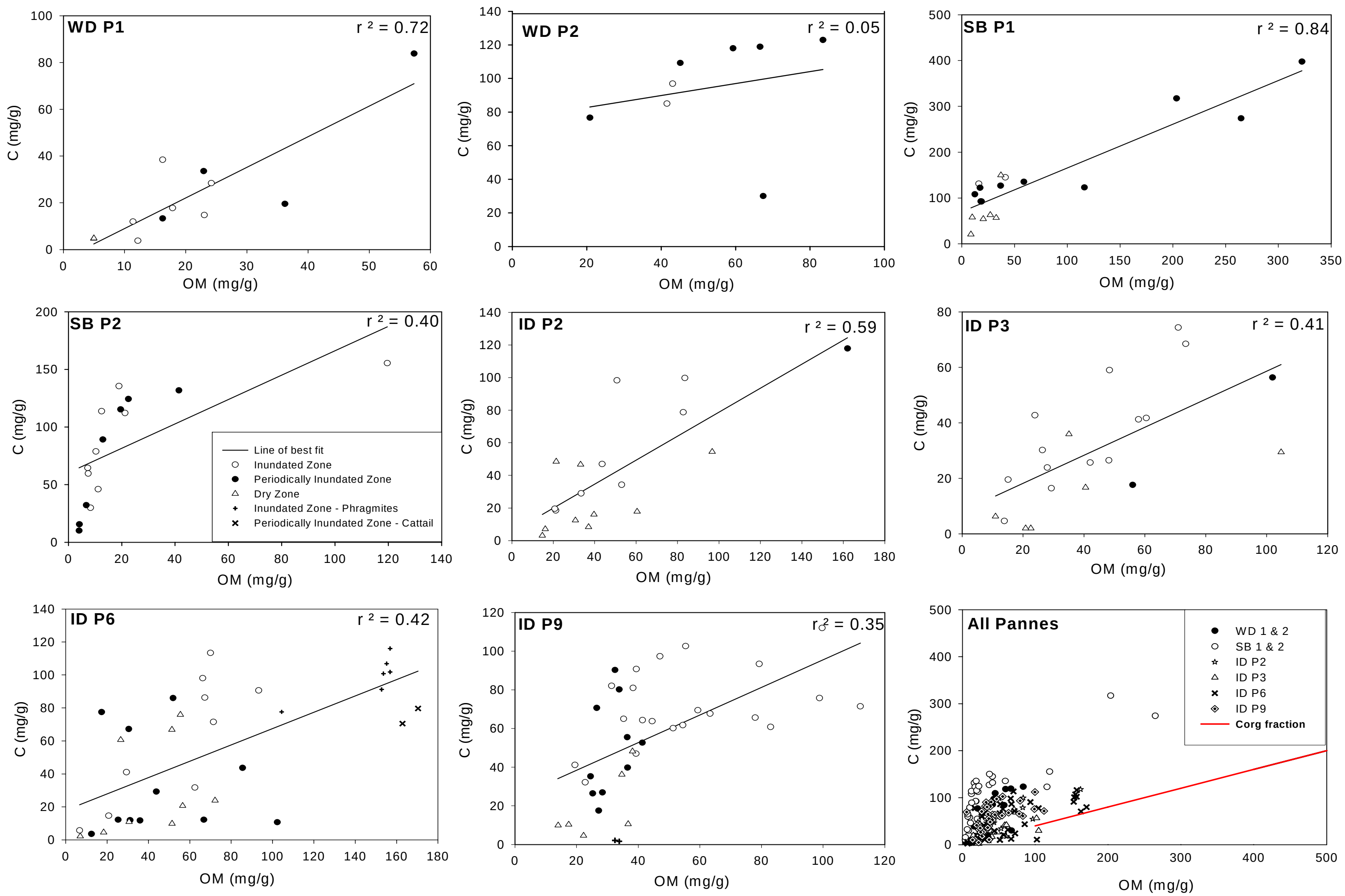


Figure 11b: Scatter plots organic Carbon content (mg/g) against total Nitrogen (mg/g) for all eight pannes in this study.

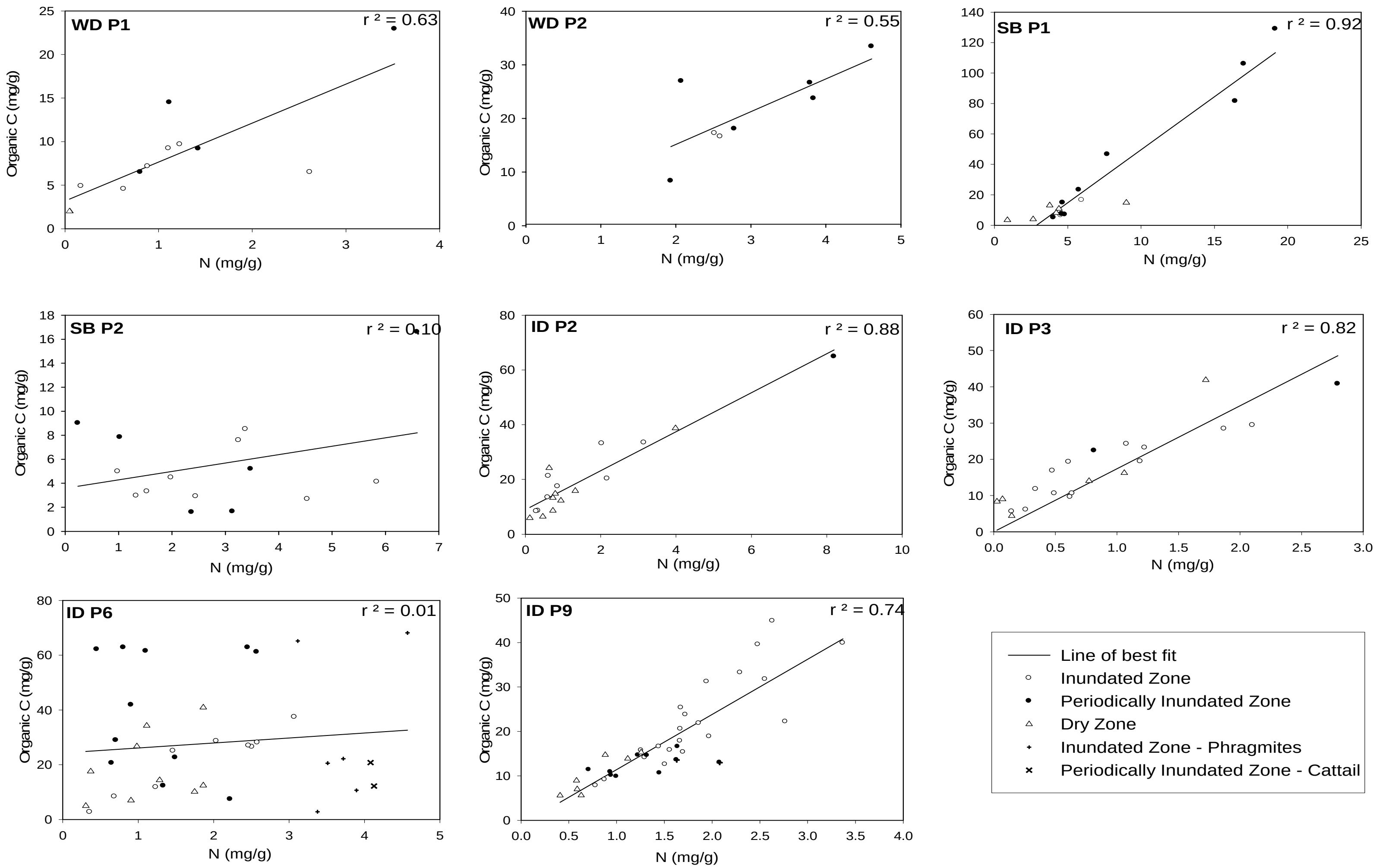


Figure 12a: Occluded Phosphorus against Fe (umol/g) across all four pannes at Indiana Dunes (step 1).

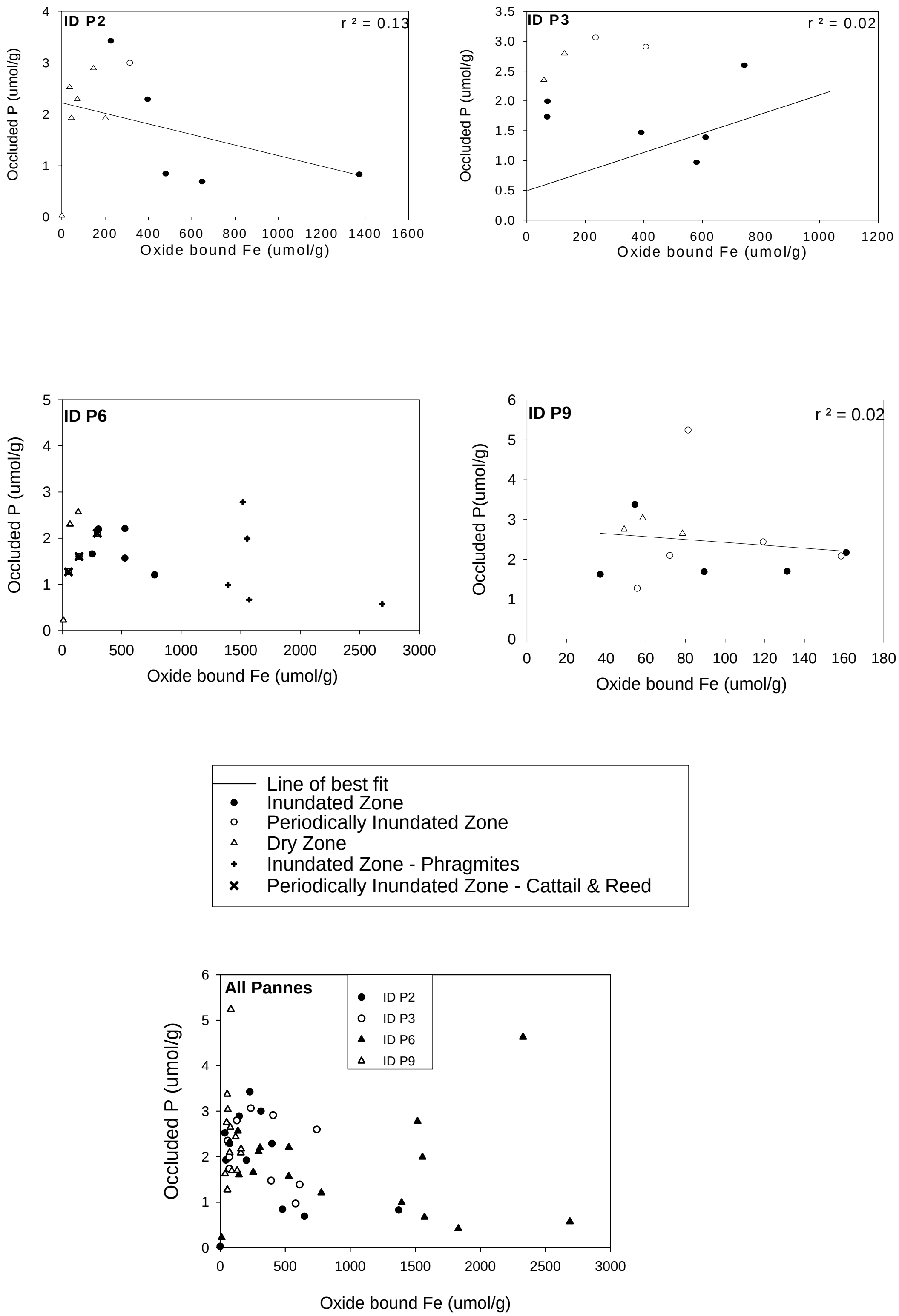


Figure 12b: Organic Phosphorus against organic matter percent across all four pannes at Indiana Dunes (step 4).

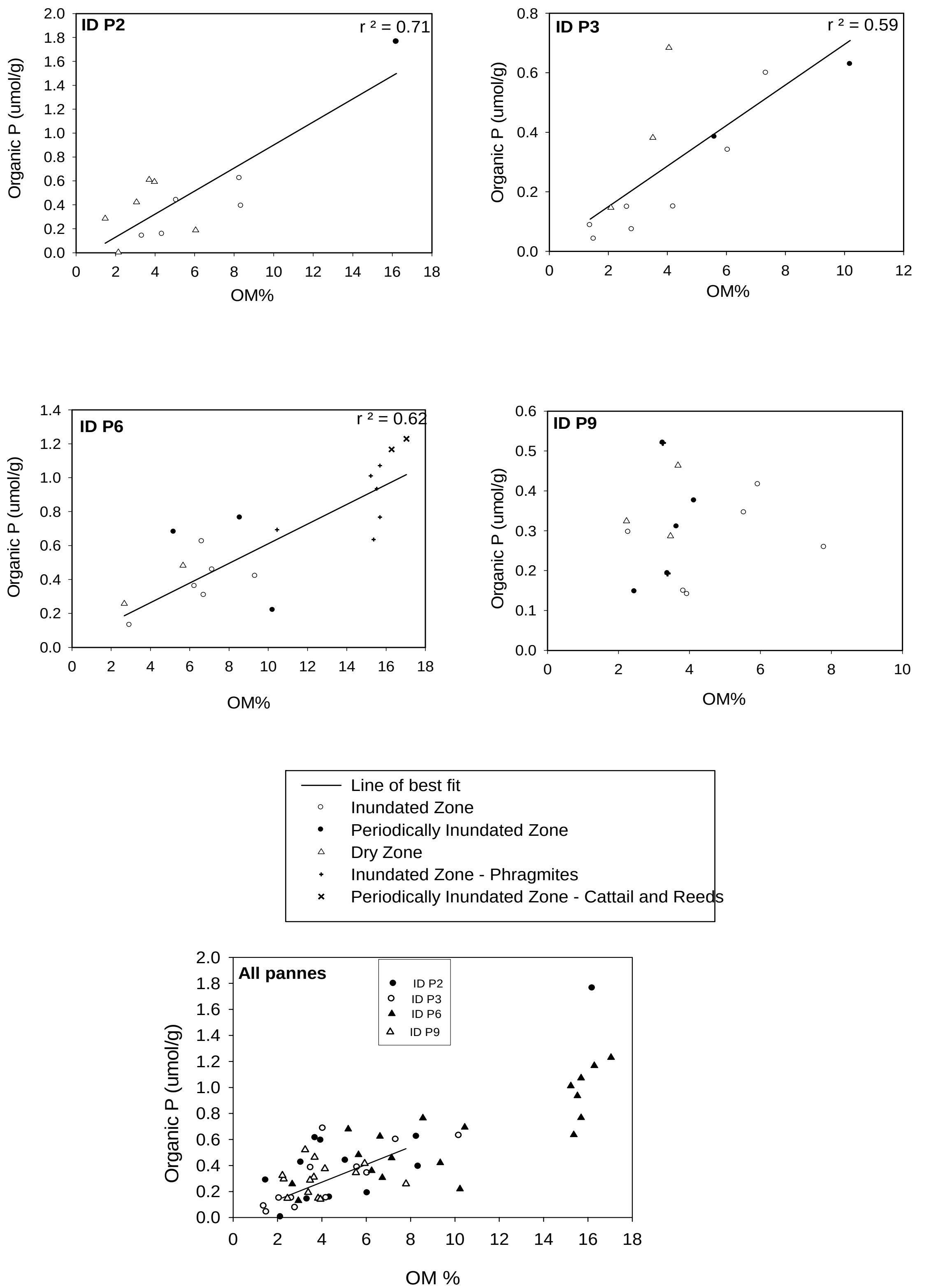


Figure 12c: Total Phosphorus (umol/g) from sequential extractions Vs organic matter percent for all four pannes at Indiana Dunes.

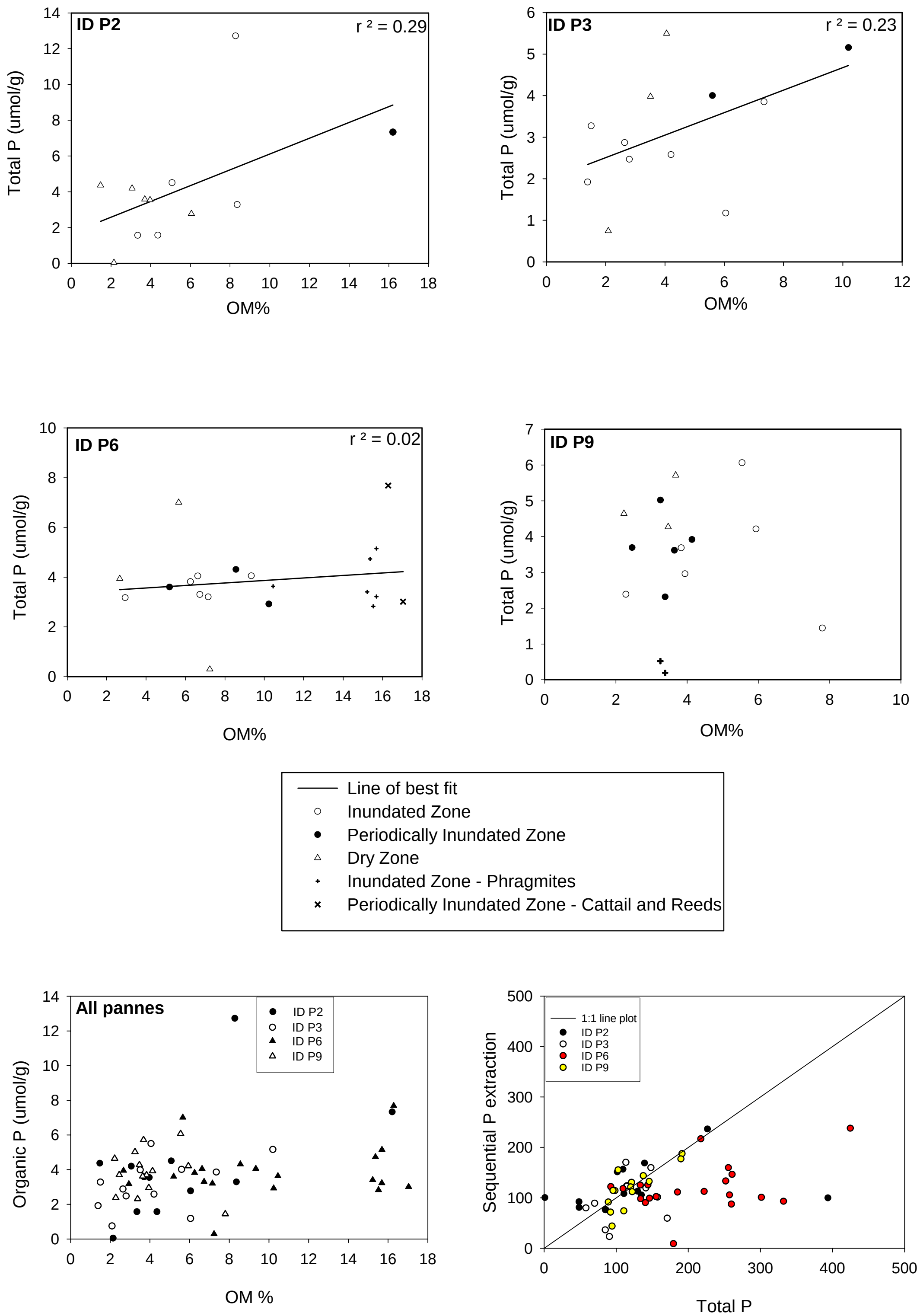


Figure 12d: Ternary Diagram representing phosphorus extractions from four pannes at Indiana Dunes along with extractions carried out on different environments from previous studies. The lake sites varied geographically and physically, with British Columbia, Laguna Zoncho, and Jackson Pond being permanently inundated small lakes, whereas Dry Lake was periodically inundated and likely is most similar to the panne sites here, although much bigger.

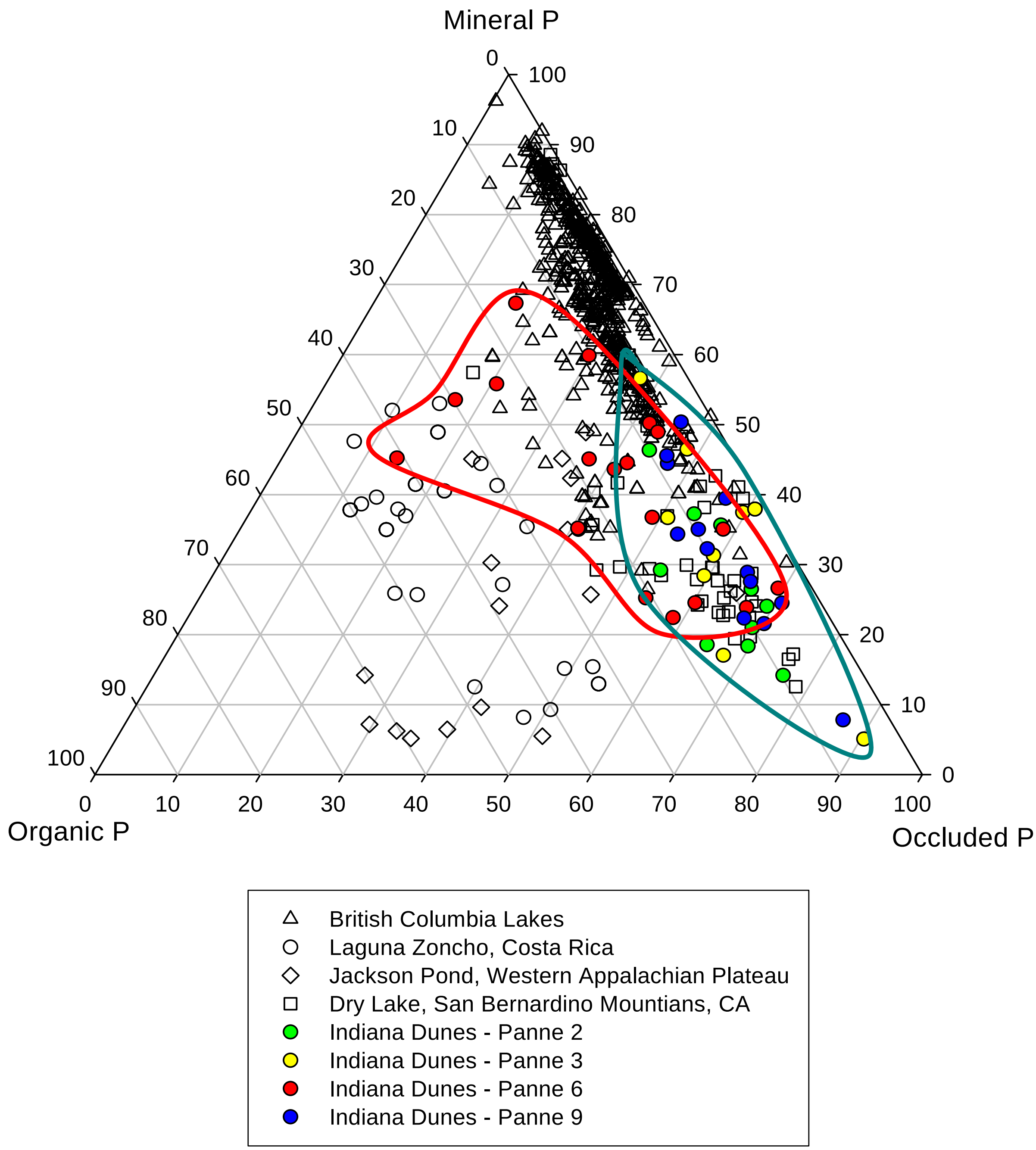
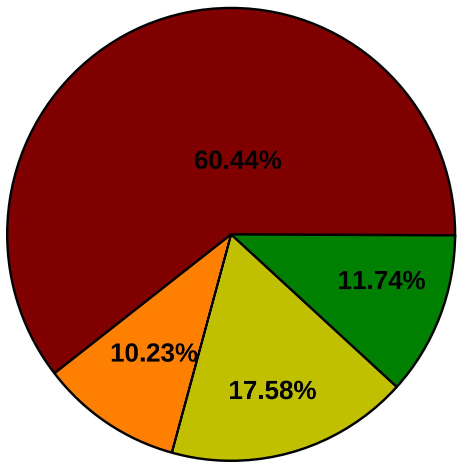
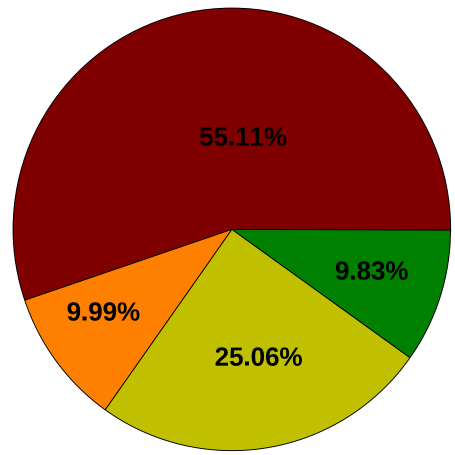


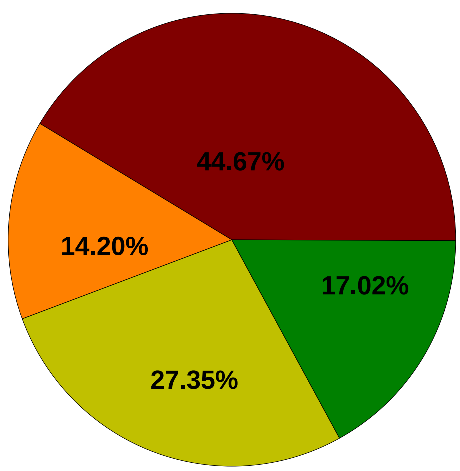
Figure 12e: Pie diagrams representing the different fc ractions of Phosphorus for pannes 2, 3, 6 and 9 at Indiana Dunes.



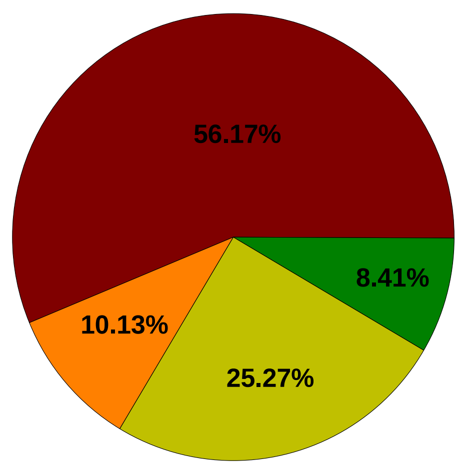
ID P2 (n = 11)	Percentage (%)	Range (%)
Occluded P	60	41 ~ 76
Carbonate P	10	6 ~ 17
Detrital P	18	8 ~ 30
Organic P	12	7 ~ 24



ID P3 (n = 12)	Percentage (%)	Range (%)
Occluded P	55	38 ~ 90
Carbonate P	10	1 ~ 26
Detrital P	25	4 ~ 49
Organic P	10	1 ~ 29



ID P6 (n = 21)	Percentage (%)	Range (%)
Occluded P	41	14 ~ 69
Carbonate P	14	7 ~ 32
Detrital P	27	9 ~ 69
Organic P	17	4 ~ 40



ID P9 (n = 14)	Percentage (%)	Range (%)
Occluded P	56	46 ~ 86
Carbonate P	10	2 ~ 28
Detrital P	25	3 ~ 53
Organic P	8	4 ~ 18

Figure 12f: Comparing National Institute of Standards Standard Reference Material Estuarine Sediment (SRM EST 1646a) data from previous sequential P extractions with extractions carried out on the pannes at Indiana Dunes.

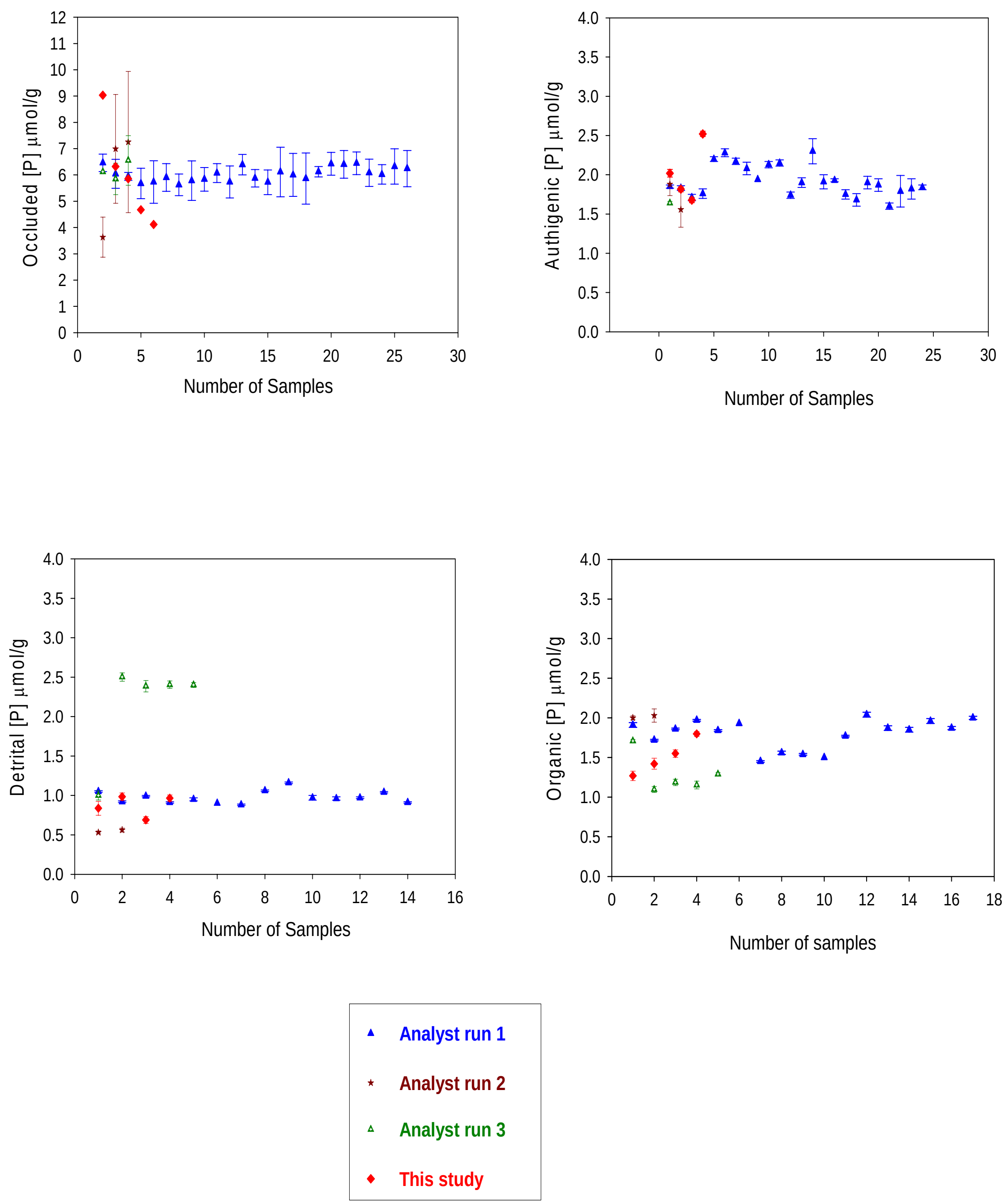


Figure 13a: Scatter plots of Fe (ppm) against organic matter (mg/g) of all eight pannes in this study.

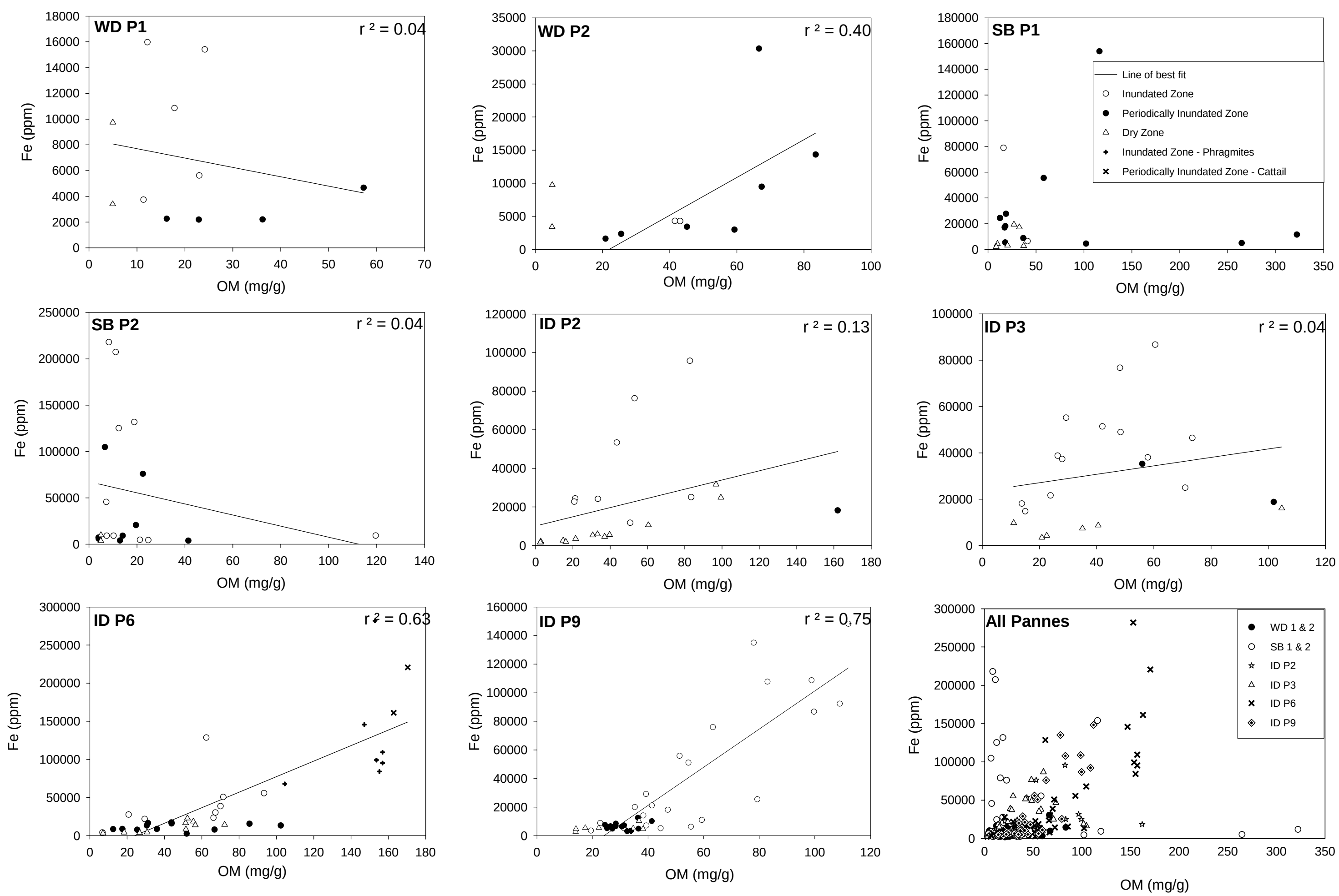


Figure 13b: Scatter plots of Cd (ppm) against organic matter (mg/g) of all eight pannes in this study.

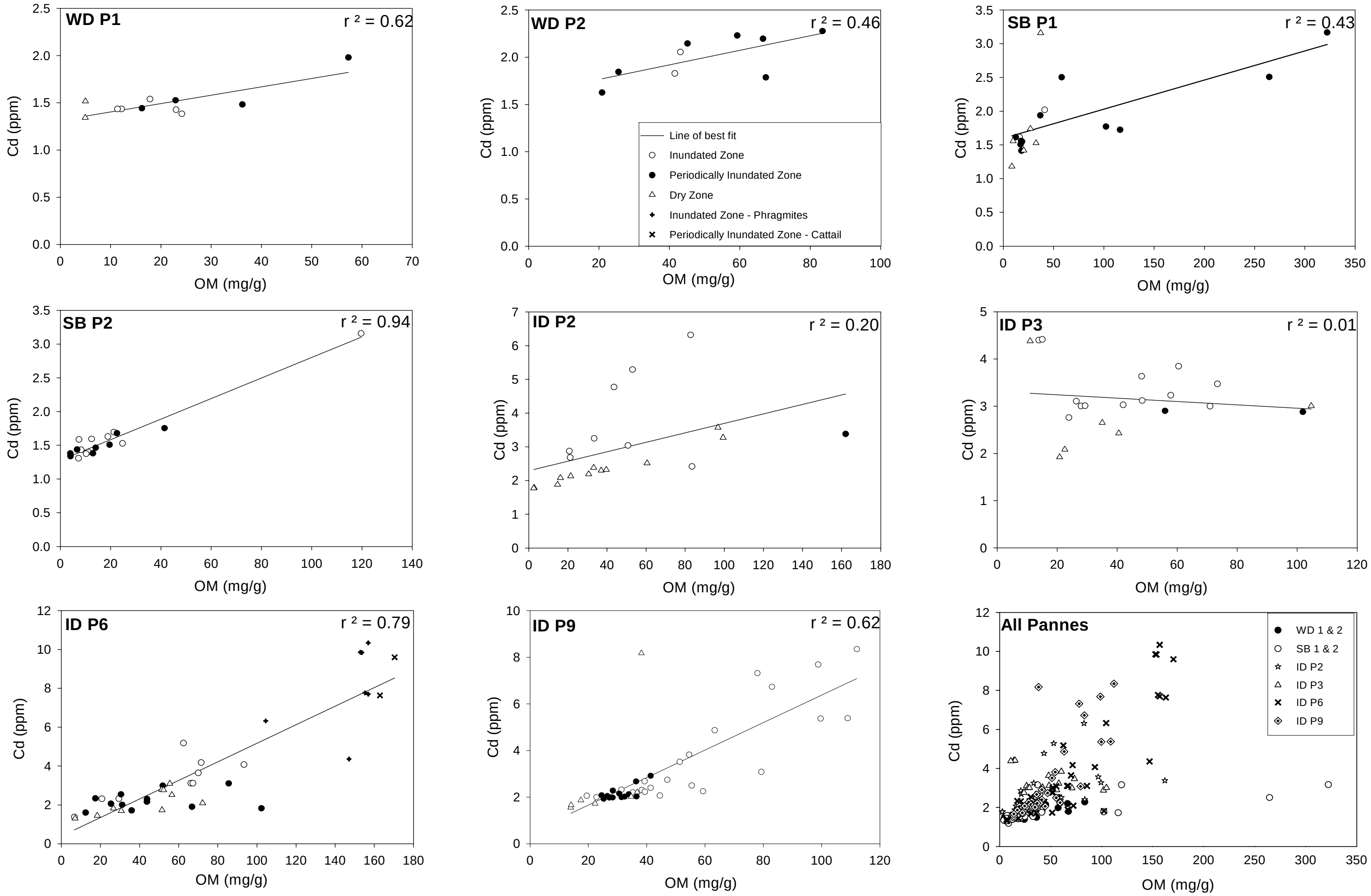


Figure 13c: Scatter plots of Cr (ppm) against organic matter (mg/g) of all eight pannes in this study.

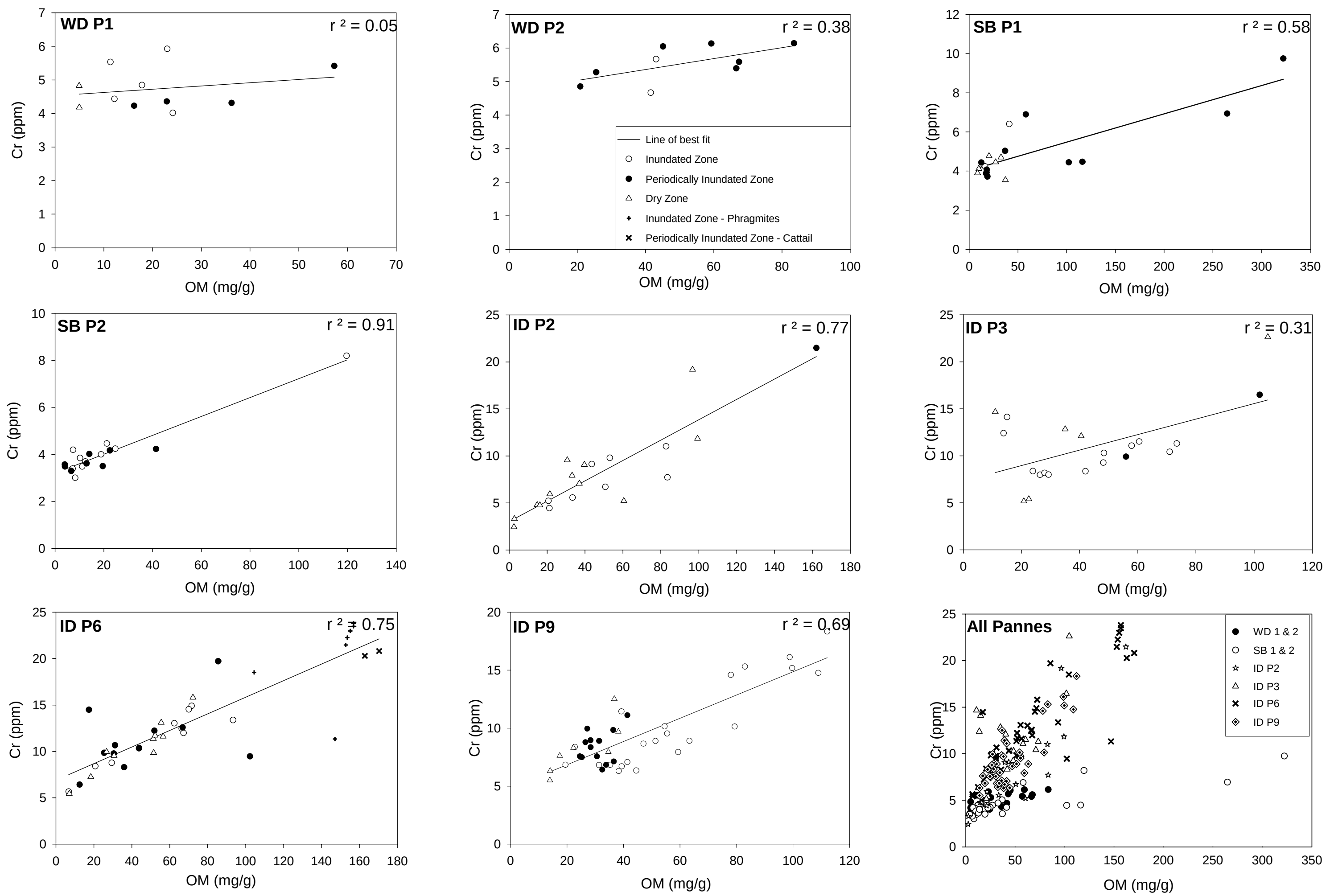


Figure 13d: Scatter plots of Cu (ppm) against organic matter (mg/g) of all eight pannes in this study.

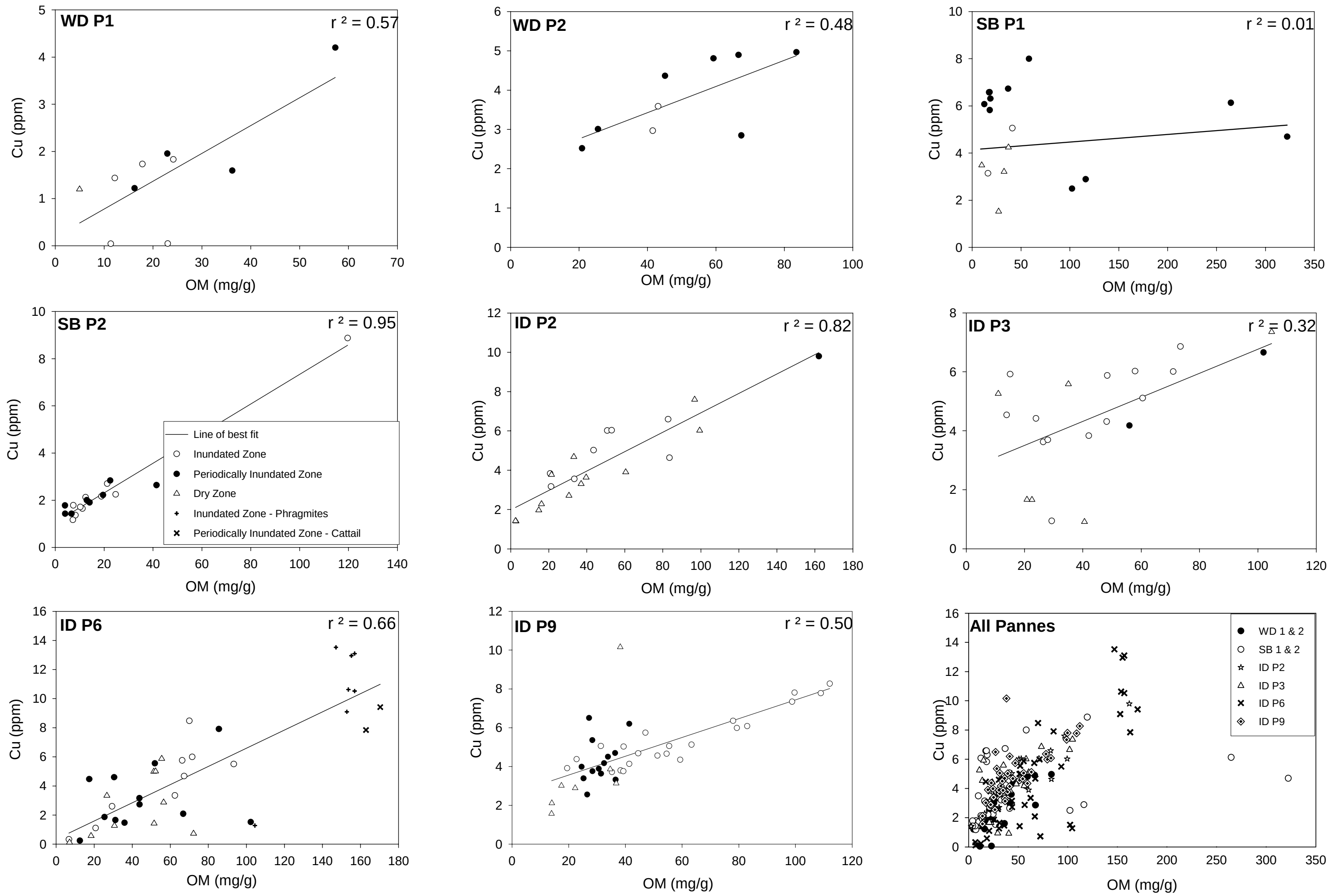


Figure 13e: Scatter plots of Ni (ppm) against organic matter (mg/g) of all eight pannes in this study.

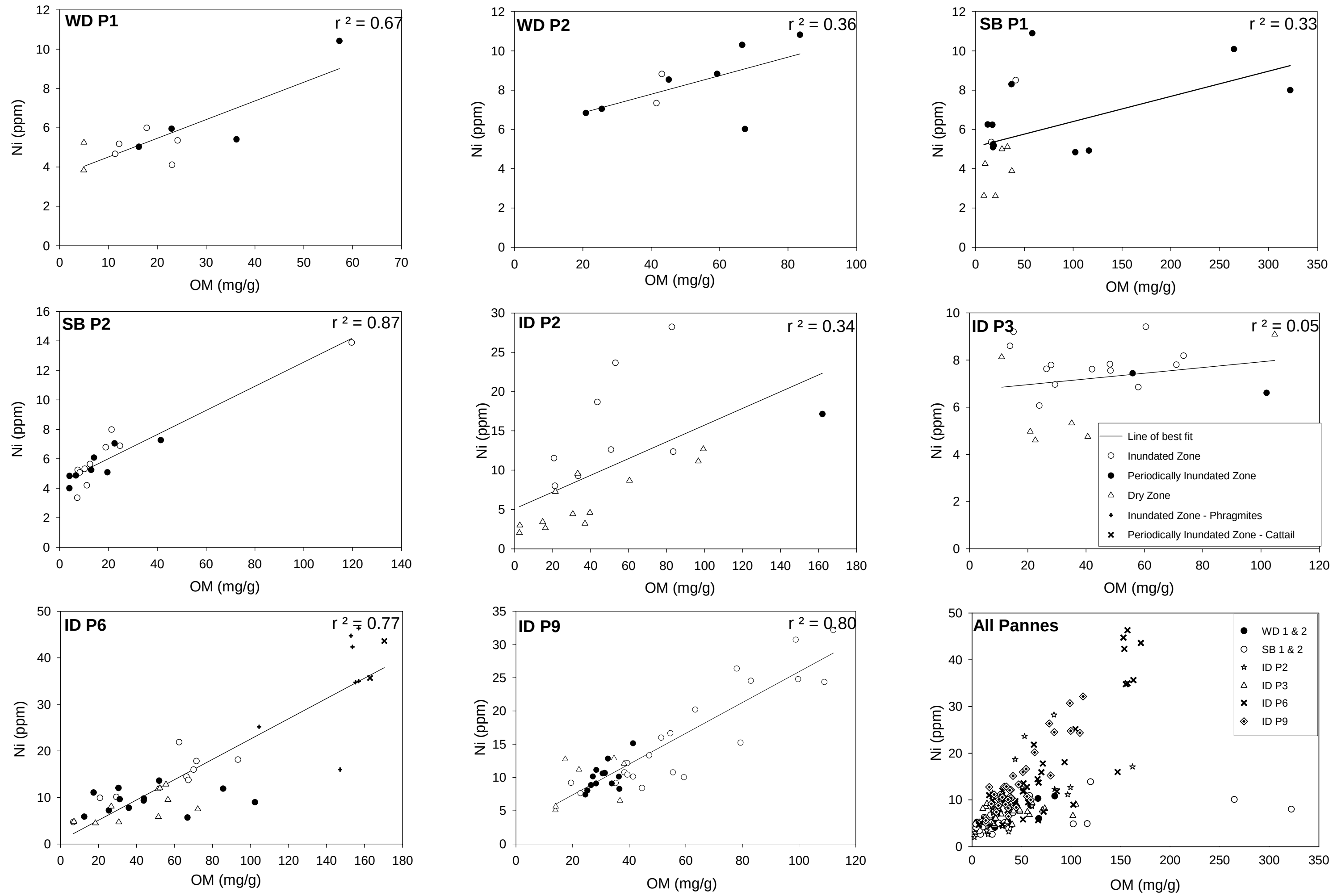


Figure 13f: Scatter plots of Pb (ppm) against organic matter (mg/g) of all eight pannes in this study.

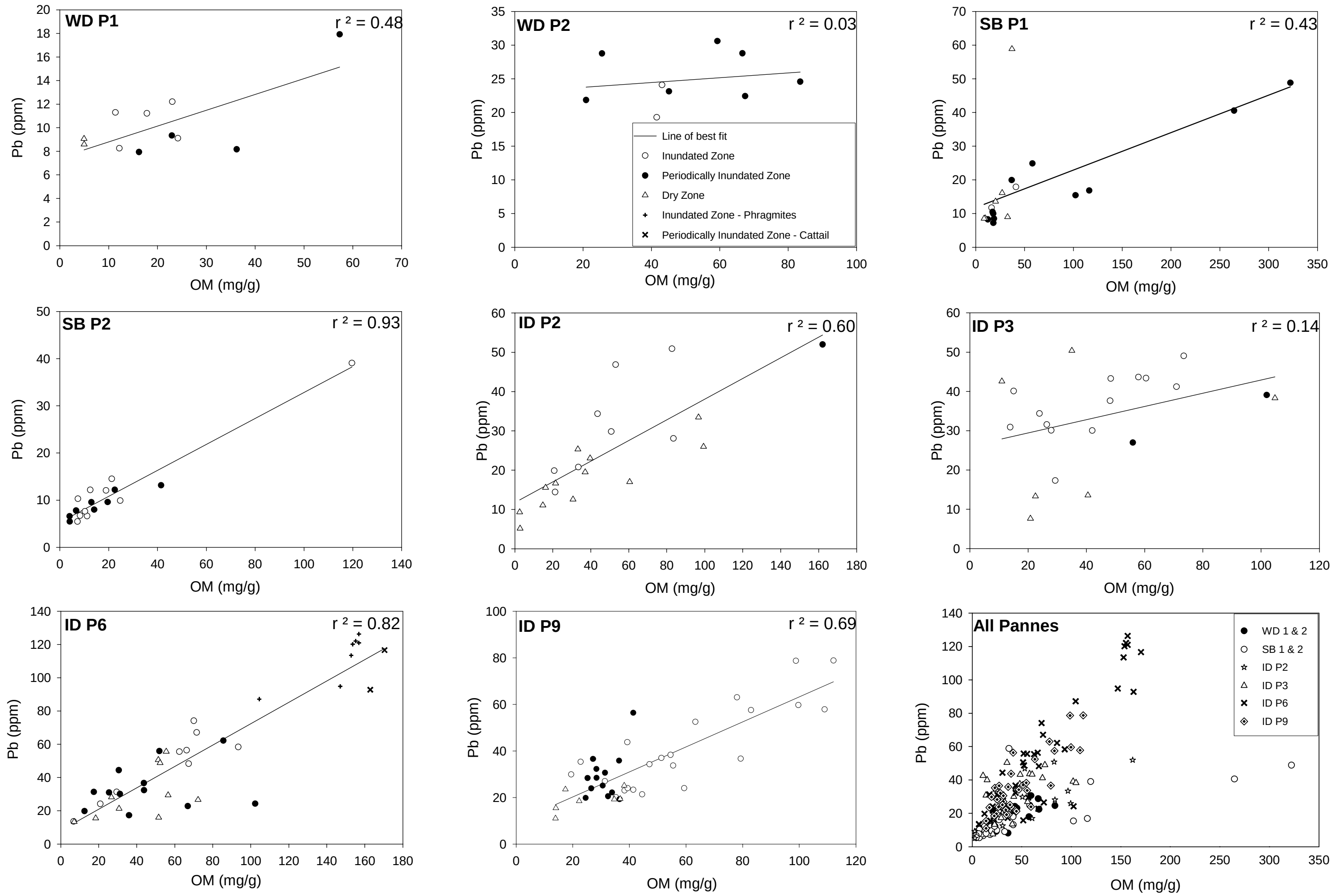


Figure 13g: Scatter plots of Ba (ppm) against organic matter (mg/g) of all eight pannes in this study.

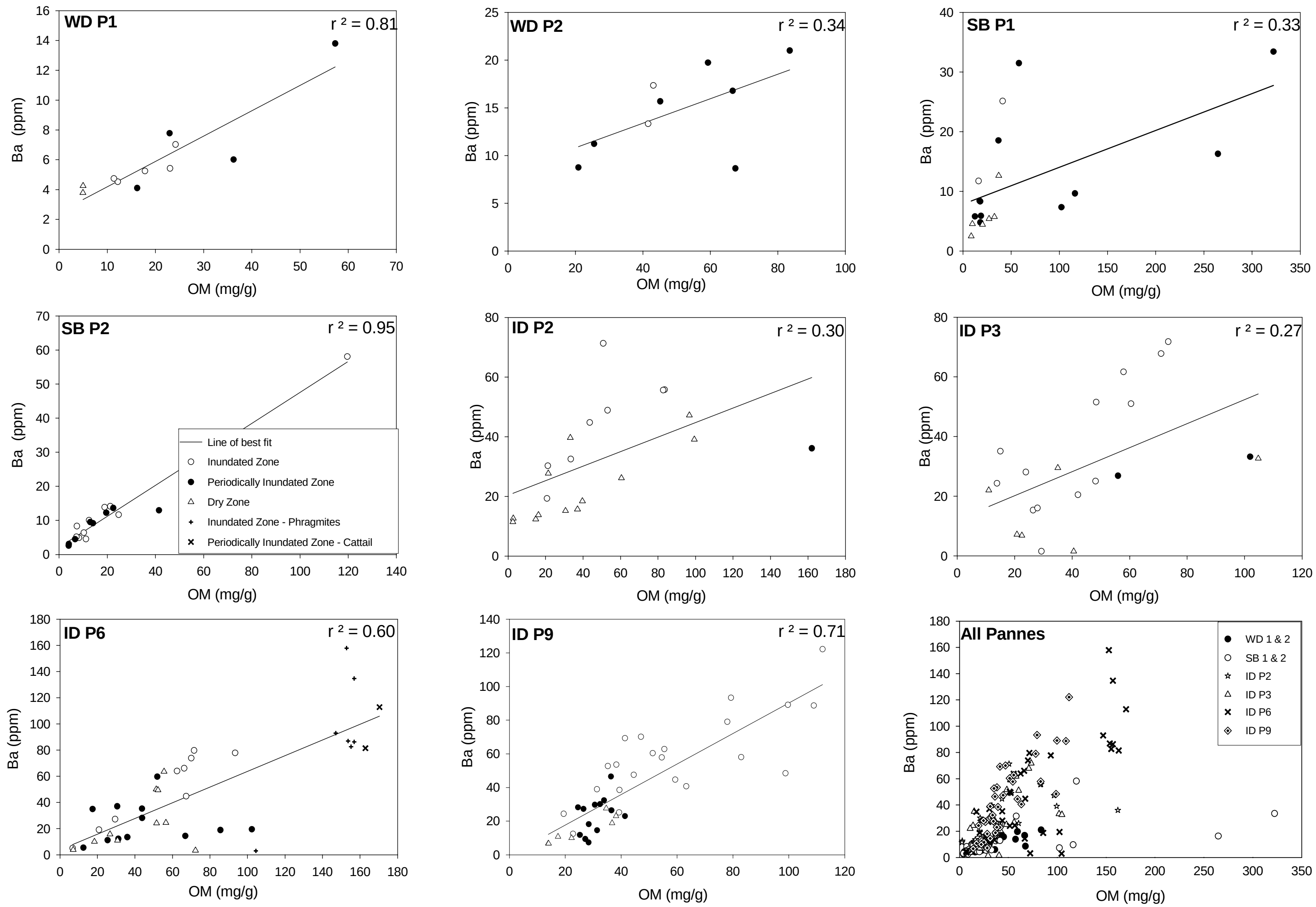


Figure 13h: Scatter plots of Mn (ppm) against organic matter (mg/g) of all eight pannes in this study.

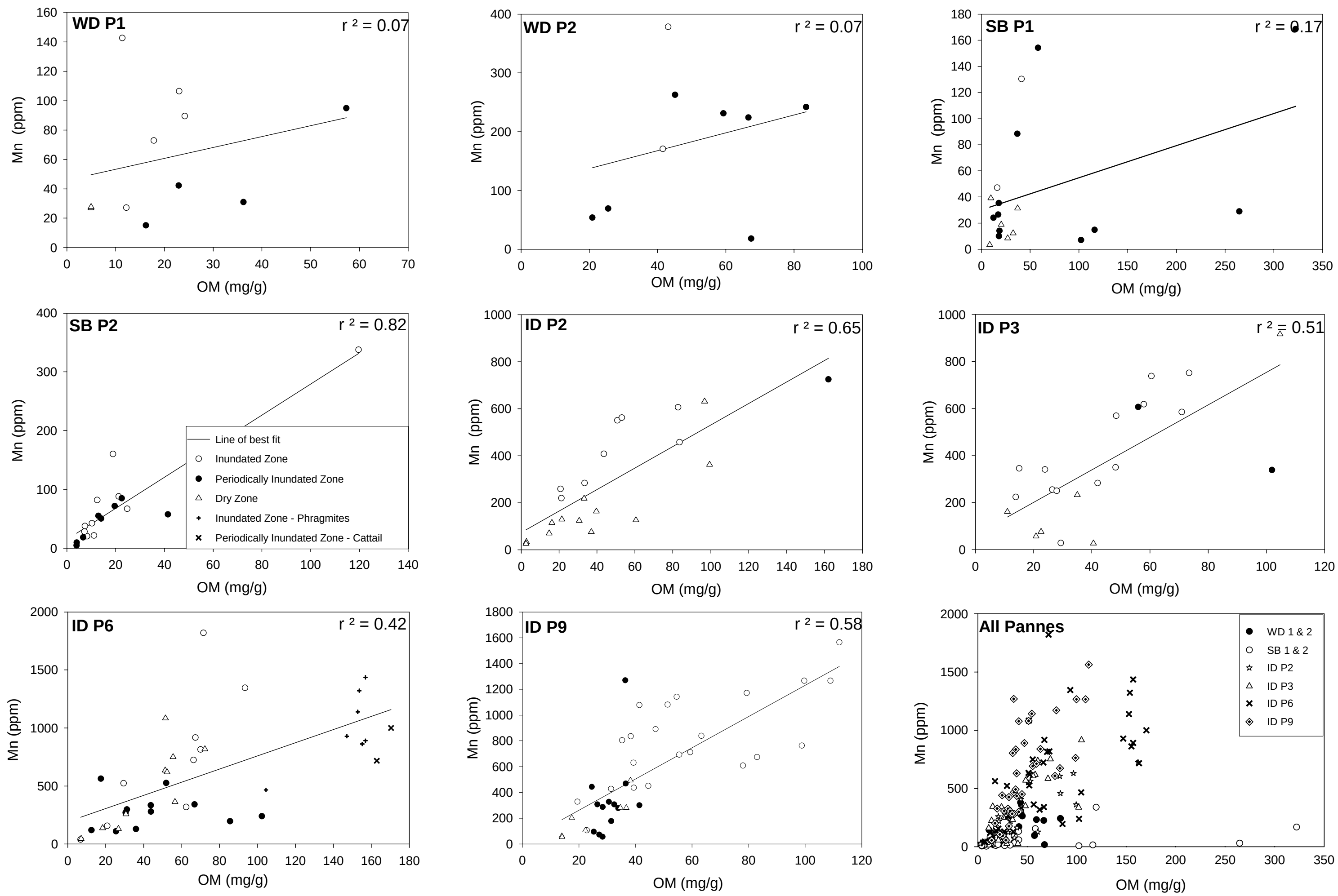


Figure 13i: Scatter plots of Zn (ppm) against organic matter (mg/g) of all eight pannes in this study.

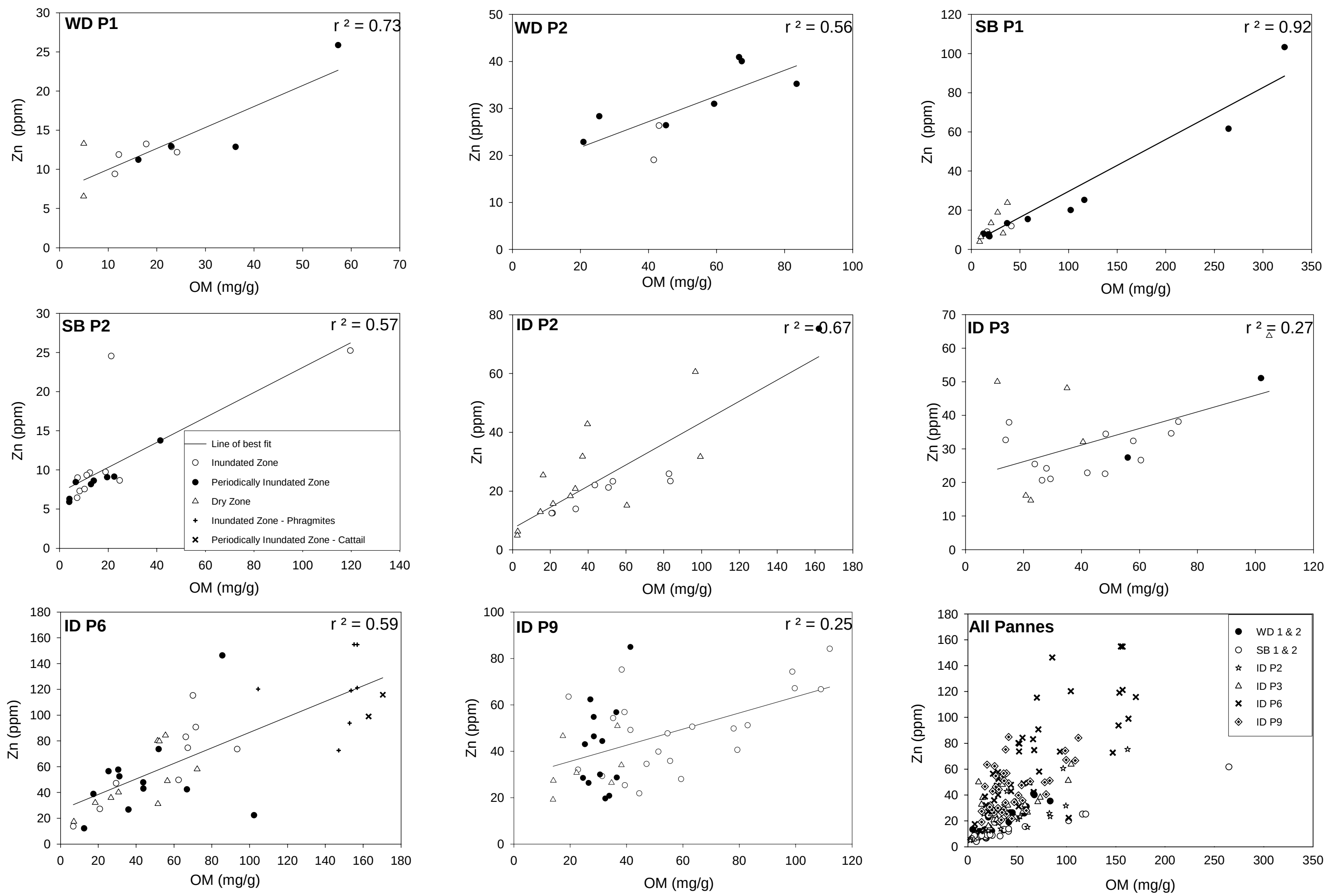


Figure 13j: Scatter plots of S (ppm) against organic matter (mg/g) of all eight pannes in this study.

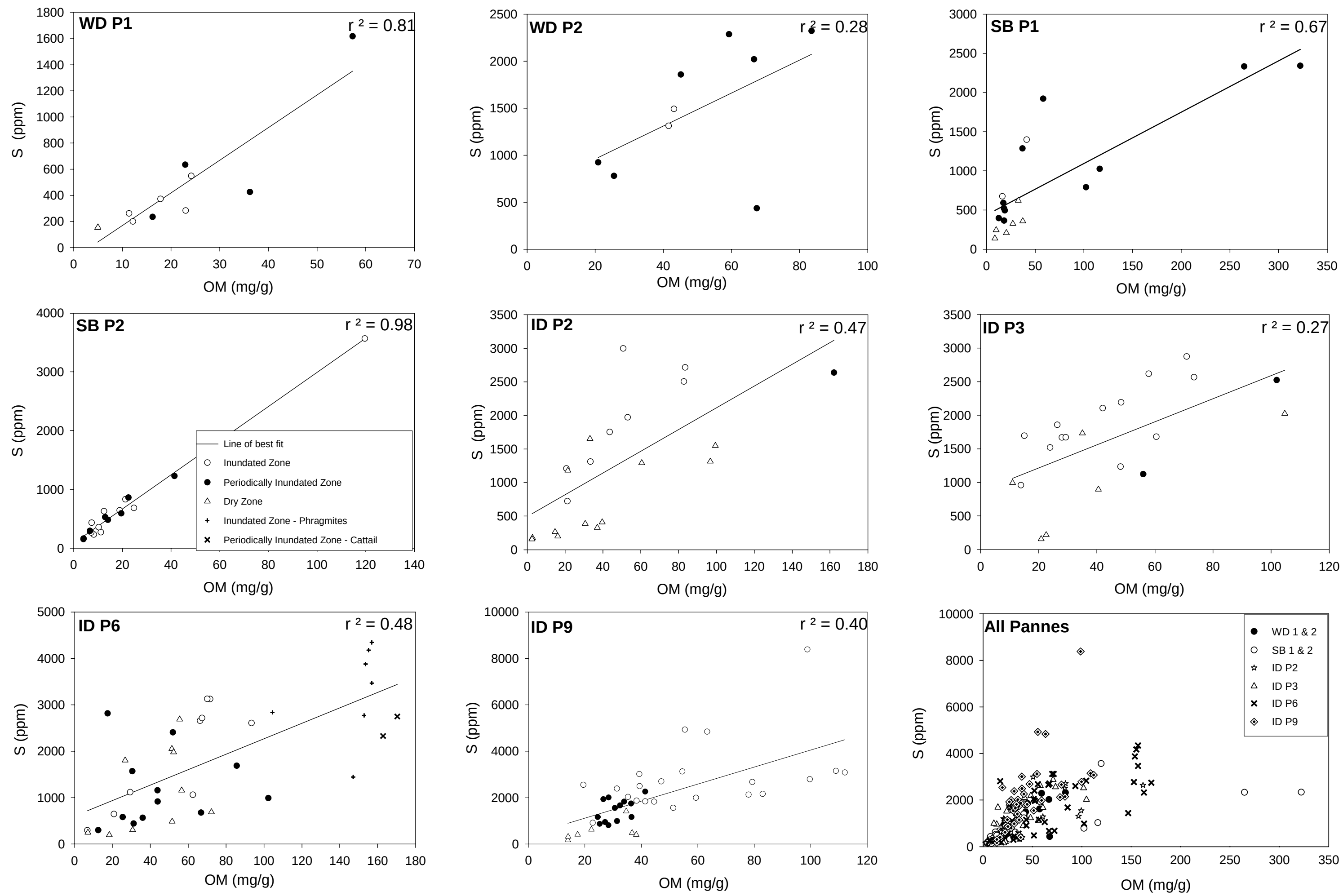


Figure 13k: Scatter plots of P (ppm) against organic matter (mg/g) of all eight pannes in this study.

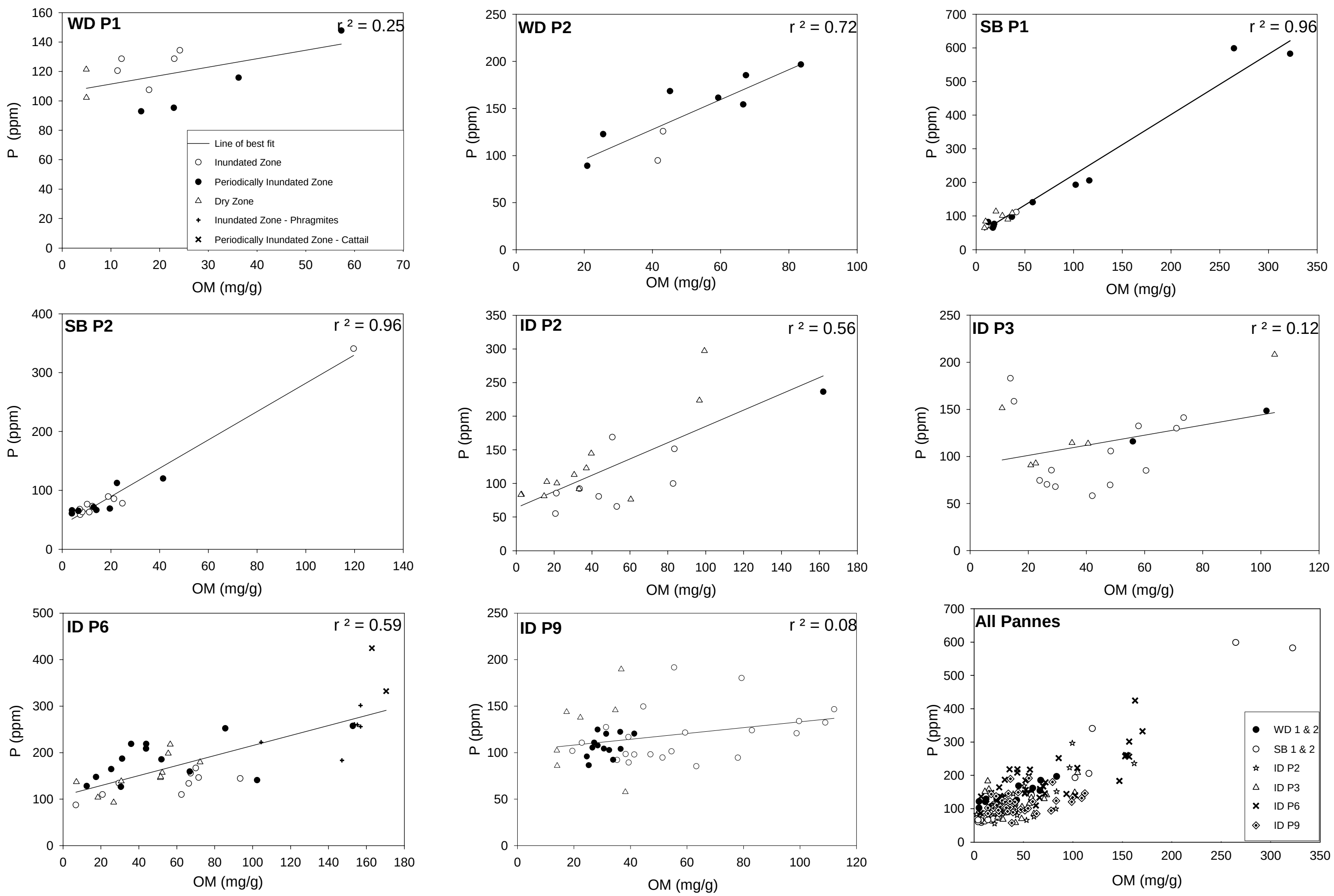
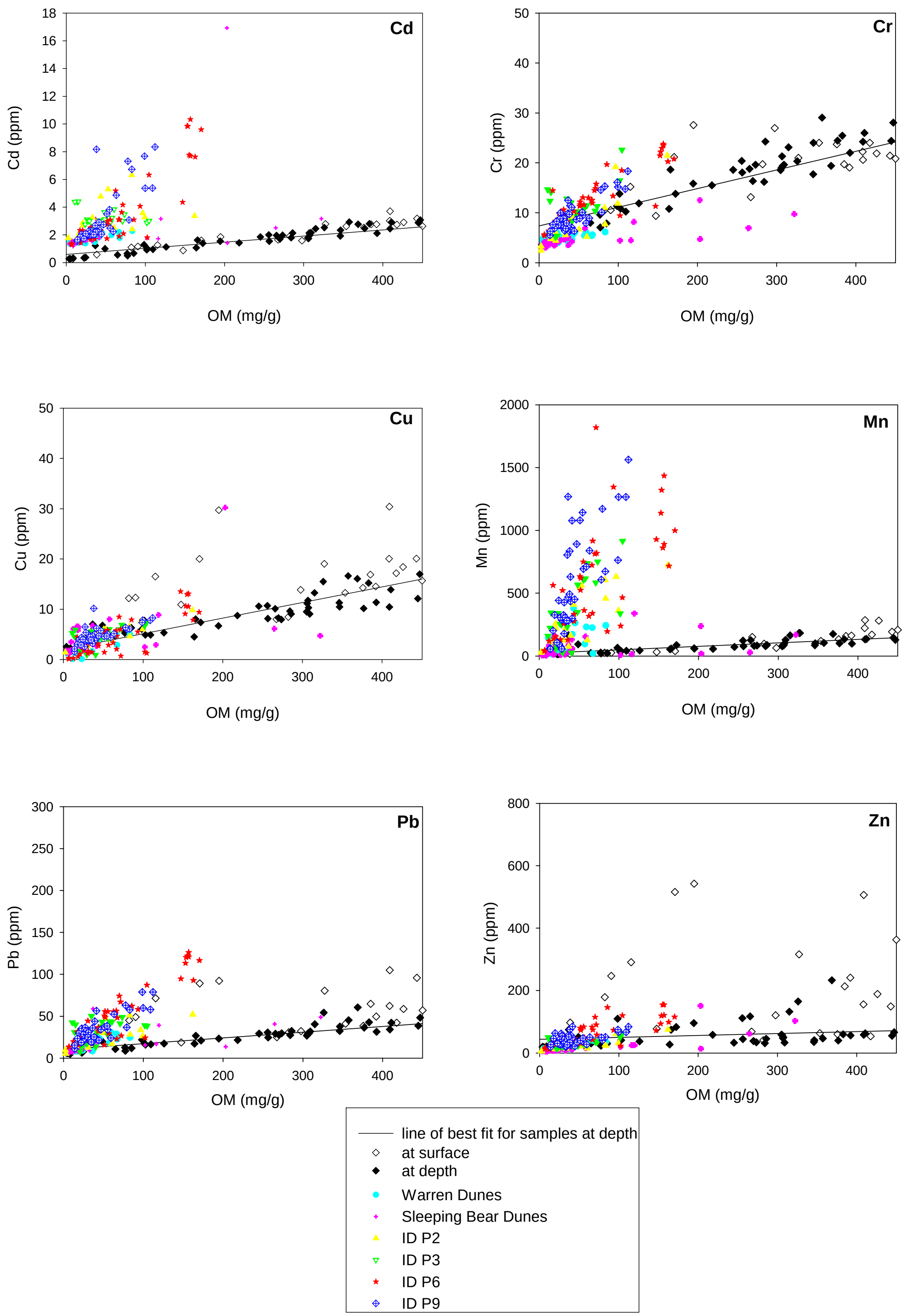


Figure 14: Scatter plots of heavy metals Vs OM (mg/g) of the pannes compared with previous studies conducted in the same area. (Accumulation rates of airborne heavy metals in wetlands).



Appendix A: Fe obtained from the ICP - AES compared to that obtained from sequential P extractions.

Sample ID	Fe obtained from Sequential P Extraction (%wt)	Fe obtained from ICP - AES (%wt)
ID - P2 - 10	0.00006	0.000056
ID - P2 - 12	0.00024	0.000094
ID - P2 - 14	0.00064	0.000330
ID - P2 - 20	0.00033	0.000207
ID - P2 - 07	0.00051	0.000319
ID - P2 - 17	0.00007	0.000080
ID - P2 - 02	0.00077	0.000425
ID - P2 - 03	0.00221	0.001682
ID - P2 - 06	0.00104	0.000938
ID - P2 - 08	0.00033	0.000186
ID - P2 - 18	0.00000	0.000064
ID - P2 - 21	0.00012	0.000104
ID - P3 - 16	0.00011	0.000076
ID - P3 - 17	0.00094	0.000254
ID - P3 - 17X	0.00128	0.000191
ID - P3 - 17Y	0.00063	0.000184
ID - P3 - 01	0.00120	0.000229
ID - P3 - 04	0.00167	0.000428
ID - P3 - 06	0.00011	0.000082
ID - P3 - 09	0.00066	0.000174
ID - P3 - 10	0.00038	0.000093
ID - P3 - 11	0.00021	0.000043
ID - P3 - 08	0.00009	0.000036
ID - P3 - 15	0.00001	0.000017

Appendix A (continued):

Sample ID	Fe obtained from Sequential P Extraction (%wt)	Fe obtained from ICP - AES (%wt)
ID - P6 - 25	0.00085	0.000125
ID - P6 - 28	0.00235	0.000318
ID - P6 - 22	0.00041	0.000058
ID - P6 - 23	0.00049	0.000054
ID - P6 - 23A	0.00085	0.000075
ID - P6 - 24	0.00126	0.000138
ID - P6 - 29	0.00376	0.000398
ID - P6 - 30	0.00295	0.000545
ID - P6 - 08	0.00011	0.000009
ID - P6 - 12	0.00022	0.000034
ID - P6 - 14	0.00002	0.000035
ID - P6 - 31	0.00210	0.000168
ID - P6 - 32	0.00245	0.000235
ID - P6 - 33	0.00253	0.000270
ID - P6 - 33A	0.00251	0.000245
ID - P6 - 34	0.00434	0.000697
ID - P6 - 18	0.00048	0.000007
ID - P6 - 03	0.00023	0.000038
ID - P6 - 05	0.00009	0.000033
ID - P9 - 3A	0.00013	0.000015
ID - P9 - 09A	0.00026	0.000035
ID - P9 - 10	0.00011	0.000017
ID - P9 - 15	0.00019	0.000027
ID - P9 - 03	0.00009	0.000022
ID - P9 - 08	0.00265	0.000333
ID - P9 - 16	0.00026	0.000025
ID - P9 - 20	0.00021	0.000031
ID - P9 - 23	0.00014	0.000018
ID - P9 - 22	0.00013	0.000025
ID - P9 - 32	0.00008	0.000013
ID - P9 - 25	0.00009	0.000013
ID - P9 - 30	0.00004	0.000008
ID - P9 - 28	0.00009	0.000008

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